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NOx ABATEMENT FOR STATIONARY SOURCES IN JAPAN

Jumpei Ando, et al

PEDCo-Environmental Specialists,
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16. ABSTRACT The report summarizes regulations for NOx abatement in Japan, describes techniques for abatement by means of combustion control, and analyzes in detail current wet and dry processes for denitrification of flue gases. The major fuel in Japan is heavy residual oil. Lesser amounts of coal are used. Natural gas usage is insignificant. Six different low-NOx oil burner designs are discussed. Eleven major NOx scrubber plants have been completed or are nearing completion. Descriptions of the major NOx removal processes are included. The chemistry of NOx liquid reactions is discussed as it applies to the various scrubber processes: advantages and disadvantages of the processes are listed. Ongoing research and development projects in Japan are also discussed.

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January 1976

PREFACE

In 1973 the Japanese government set an ambient standard for nitrogen oxides (NO_x) that is more stringent than that in any other country of the world: 0.02 ppm daily average. Regulations pertaining to NO_x emissions in motor vehicle exhausts are in preparation. Emission standards for waste gases from stationary sources are to be attained by mid-1975 by means of combustion control and removal of NO_x from tail gases of nitric acid plants. Thus, with promulgation of the ambient standard and of regulations to limit emissions from both mobile and stationary sources, the responsible authorities are taking firm steps toward NO_x abatement. A serious problem, however, is that the ambient standard is still far out of reach in Japan, where energy consumption per unit area of level land is 8 times that in the United States and may be the highest in the world.

Because most people believe that attaining the ambient standard will require removal of NO_x from flue gases (denitrification), many organizations have started to develop NO_x removal processes. Regulative action by local governments, which tend to impose even more stringent regulations than does the central government, is forcing industries to install flue gas denitrification facilities. As these facilities are operated, however, we find that denitrification apparently is more difficult than desulfurization, for which technologies are well-developed in Japan. In addition to the technical difficulties of denitrification, there is some

doubt as to whether the stringent ambient standard is really necessary for protecting human health. Despite these concerns, several commercial plants for flue gas denitrification have started operation and many others are under construction.

This report summarizes briefly the regulations for NO_x abatement in Japan, describes techniques for abatement by means of combustion control, and analyzes in detail the current technologies of denitrification by wet and dry processes.

The information reflects technology and economics current in January 1975.

CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

The metric system is used in this report. Some of the factors for conversion between the metric and American systems are shown below:

1 m (meter) = 3.3 feet
1 m^3 (cubic meter) = 35.3 cubic feet
1 t (metric ton) = 1.1 short tons
1 kg (kilogram) = 2.2 pounds
1 liter = 0.26 gallon
1 kl (kiloliter) = 6.29 barrels
1 kcal (kilocalorie) = 3.97 Btu

The capacity of NO_x removal systems is expressed in normal cubic meters per hour (Nm^3/hr). One Nm^3/hr = 0.59 standard cubic foot per minute. For monetary conversion, the exchange rate of 1 dollar = 300 yen is used.

ABBREVIATIONS

SCR	Selective catalytic reduction
MW	Megawatt
kW	Kilowatt
SV	Space velocity

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1. STATUS OF NO_x ABATEMENT IN JAPAN

REGULATIONS

Ambient Air Quality Standard

An ambient standard for NO_2, based on a recommendation by the Special Committee of the Central Council on Environmental Pollution Control, was set forth by the Cabinet and announced by the Environment Agency in May 1973. The standard requires that ambient concentrations of NO_2 be kept below 0.02 ppm (about 0.04 g/Nm^3) in a daily average of hourly values; conformance with this standard is to be attained within 5 years in most districts and within 8 years in heavily polluted cities such as Tokyo and Osaka.

Compared with the national ambient standard in the United States Standard (0.05 ppm yearly average, which is close to 0.1 ppm daily average) and also with the German standard, which approximates that in the United States, the Japanese standard is very stringent. NO_2 concentrations in large cities such as Tokyo and Osaka normally range from 0.03 to 0.04 ppm. In January 1975 the Environment Agency reported that in only 3 cities among 147 was the NO_2 level as low as 0.02 ppm or lower.

A motive for the stringent regulation was the frequent occurrence of photochemical smog in Tokyo in 1972 (described in a 1973 report).[1] The smog, however, may not be similar to that in California, which occurs at much higher NO_x concentrations. Moreover, fewer warnings for photochemical smog were issued last year than in 1972 in spite of a slight increase in NO_2 concentrations. For these reasons it may be

desirable to reevaluate the ambient standard on the basis of additional scientific data, including medical data. Relaxing the standard, however, would probably be difficult in Japan, where the people are deeply concerned with environmental pollution.

Emission Standards

In August 1973 emission standards for NO_x were promulgated for large stationary sources, classified as shown in Table 1-1. These standards take into account the status of abatement technology and are similar to those in the United States. The emission standards may well be achieved in 1975.

The problem is, however, that several local governments limit emissions of NO_x from new plants to very low levels. These limitations impose severe constraints upon construction of new NO_x- emitting facilities, such as electric power plants.[3]

Total Quantity Control

A supplement to the Air Pollution Control Law was published in June 1974, as a "total quantity control law," designed to attaint the ambient standards by control of pollutants from fuel burning, i.e. SO_x, NO_x, and particulates. This law is summarized as follows:

1) The Environment Agency designates the pollutants and areas to which this law is applied. These are called "designated pollutants," and "designated areas."

2) The governers of local governments must determine the necessary reduction of the designated pollutants to achieve ambient standards in the designated areas.

Table 1-1. NO_x EMISSION STANDARDS (August 1973)

		NO_x, ppm		Applicable capacity, Nm^3/hr	Time limit	O_2 in gas, %
		New	Existing			
Boiler	Gas fuel	130	170	40,000 for new plants, 100,000 for existing ones	2 years for existing plants	5
	Solid fuel	480	600			6
	Low grade coal		750			
	Liquid fuel	180	230			4
	Crude tar		280			
Metal heating furnace		200	220	10,000 for new plants, 40,000 for existing ones		11
Oil heating furnace		170	210			6
Nitric acid plant		200	200	All	3 years	--

In September 1974 the agency designated 11 areas, including Tokyo and Osaka; it will add another 11 in the near future. SO_2 was selected as the first designated pollutant, for which the new ambient standard (0.04 ppm daily average, published in 1973) must be attained by the end of 1977. NO_x and particulates are to be designated soon. Under the control law it is not possible in a designated area to build a new plant without shutting down old ones or vastly reducing pollutant emissions from both old and new plants.

The required reduction of SO_2 emissions may be attained by using expensive low-sulfur fuels or by applying flue gas desulfurization, a technology that is well-developed in Japan. Reduction of NO_x emissions is much more difficult. Nevertheless, several local governments such as Tokyo, Osaka, Chiba, and Mie are preparing their own NO_x regulations for total quantity control, which could be even more stringent than the national regulations. The authors believe that the national ambient standard for NO_x should be reevaluated before these local NO_x control regulations are established.

NO_x Control for Motor Vehicle Exhausts

Control of NO_x emissions in motor vehicle exhausts to a level of 0.25 g/km or 0.40 g/mile was originally scheduled for 1976. After several meetings in late 1974, however, the Special Committee of the Central Council on Environmental Pollution Control concluded that scheduled enforcement of the maximum permissible limit should be postponed 2 years owing to the technical difficulty involved, and that the temporary limits should be 0.85 g/km for large cars (weighing over 1000 kg) and 0.6 g/km for small cars. Very recently the Director-General of the Environment Agency recommended

to the Minister of Transportation that the temporary limit be set at 1.2 g/km, a value obtained by adding 40 percent to the 0.85 g/km standard to account for fluctuations in engine quality. The 1.2 gram limit is the same as that now practiced in California.

Some automobile manufacturers, such as Honda, Matsuda, and Mitsubishi, have developed engines that yield low NO_x emissions; however, two major manufacturers, Toyota and Nissan, claim that it is technically impossible to supply by 1976 new engines with NO_x emissions under 0.9 g/km without a substantial increase in fuel consumption.

Overview of NO_x Abatement Technology

Technologies under development in Japan for control of NO_x are similar to those being developed in the United States: combustion control, use of low-NO_x burners, two-stage combustion, off-stoichiometric combustion, and flue gas recirculation. These and other NO_x control techniques are under consideration and active development by many groups including boiler manufacturers, electric power companies, national research institutes, and universities.

Because the emission standards for stationary sources must be attained by the summer of 1975, the control methods are being applied to the larger-capacity plants. In addition, heavy oil, containing 0.1 to 0.4 percent nitrogen, which has been the major fuel in Japan, has been replaced by low-nitrogen oil or gas in many plants.

The Environment Agency estimates that even when 60 percent of the NO_x is reduced by control of combustion and a change of fuel, about 20 percent of the total flue gas should be treated to remove 90 percent of the NO_x by 1978, and 30 percent should be treated by 1981 in order to attain the ambient standard. The central and local governments are

trying to promote the development of NO_x removal technology by providing research funds and extending low-interest loans for constructing NO_x removal plants. Further, the Japan Iron and Steel Federation has established a $10 million fund to promote basic and applied research on countermeasures for NO_x control.

Among various processes for flue gas denitrification, dry catalytic reduction of NO_x by ammonia is typically used in the presence of negligible amounts of SO_x and particulates. The reduction process, however, can be used to treat dirty flue gas containing SO_x and particulates, but not without additional difficulty. Wet processes using scrubbers have also been developed. The wet processes, however, may be more difficult than catalytic reduction limestone or lime, the cheapest absorbents useful for removal of SO_2, is not used for removal of NO_x, which is less reactive than SO_2. Moreover most of the wet processes entail treatment of wastewater containing nitrates or nitrites. Some of them, however, offer the advantage of simultaneous removal of SO_x and NO_x.

Technologies for abatement of NO_x from stationary sources are described in detail in the following sections.

2. COMBUSTION CONTROL

BACKGROUND

Fuel in Japan

Heavy oil, residue of atmospheric distillation of crude oil, has been the major fuel in Japan. In 1973 consumption of heavy oil was about 140 million tons, while combustion of coal as fuel was about 25 million tons. By comparison use of domestic natural gas and imported LNG is still insignificant, although use of the latter is fast increasing.

The nitrogen contents of heavy oil, coal, and kerosene are shown in Table 2-1. As is well-known, normally about 30 percent of the nitrogen is converted into NO_x on combustion and is emitted together with thermal NO_x formed by the reaction of nitrogen in air with oxygen. The major fuels used until recently were grades B and C heavy oils, relatively rich in nitrogen. Use of grade A oil, kerosene, and natural gas has increased since the NO_x emission standards were set forth, although those low-nitrogen fuels are expensive.

Table 2-1. NITROGEN CONTENT OF FUELS

Fuel		Nitrogen content, %
Heavy oil	grade A	0.005 - 0.08
	grades B, C	0.08 - 0.35
Coal		0.5 - 2.5
Kerosene		less than 0.005

Combustion Modification

Figure 2-1 shows results of an opinion survey concerning combustion modification methods; the survey covered about 100 plants, involving mainly industrial boilers and some utility boilers and furnaces. Next to the change of fuels, use of low-NO_x burners is the preferred control method. Staged combustion and flue gas recirculation have been adopted widely for utility boilers but not much for industrial boilers because of the high investment costs.

Characteristics of the combustion modification methods are summarized in Table 2-2. Although these methods are the most useful and practical for NO_x abatement, they have some disadvantages: they decrease heat efficiency, require large installations, and increase emissions of other pollutants. Their efficiency for NO_x abatement is naturally limited by the necessity of minimizing these problems.

NIPPON FURNACE LOW-NO_x BURNERS

Background

The developer is Nippon Furnace Kogyo Kaisha Ltd., one of Japan's largest burner and furnace makers. Nippon Furnace, has developed two types of low-NO_x burners: one is the TRW type suitable for boilers, which has been commercialized under a technical license agreement with Civiltech Corp. (U.S.) in a joint venture with TRW, Inc.; the other is a self recirculating gasification (SRG) burner, an original product suitable for heating furnaces.

TRW TYPE BURNER

Description

This burner is designed to attain good mixing of air and fuel, with rapid combustion. As shown in Figure 2-2,

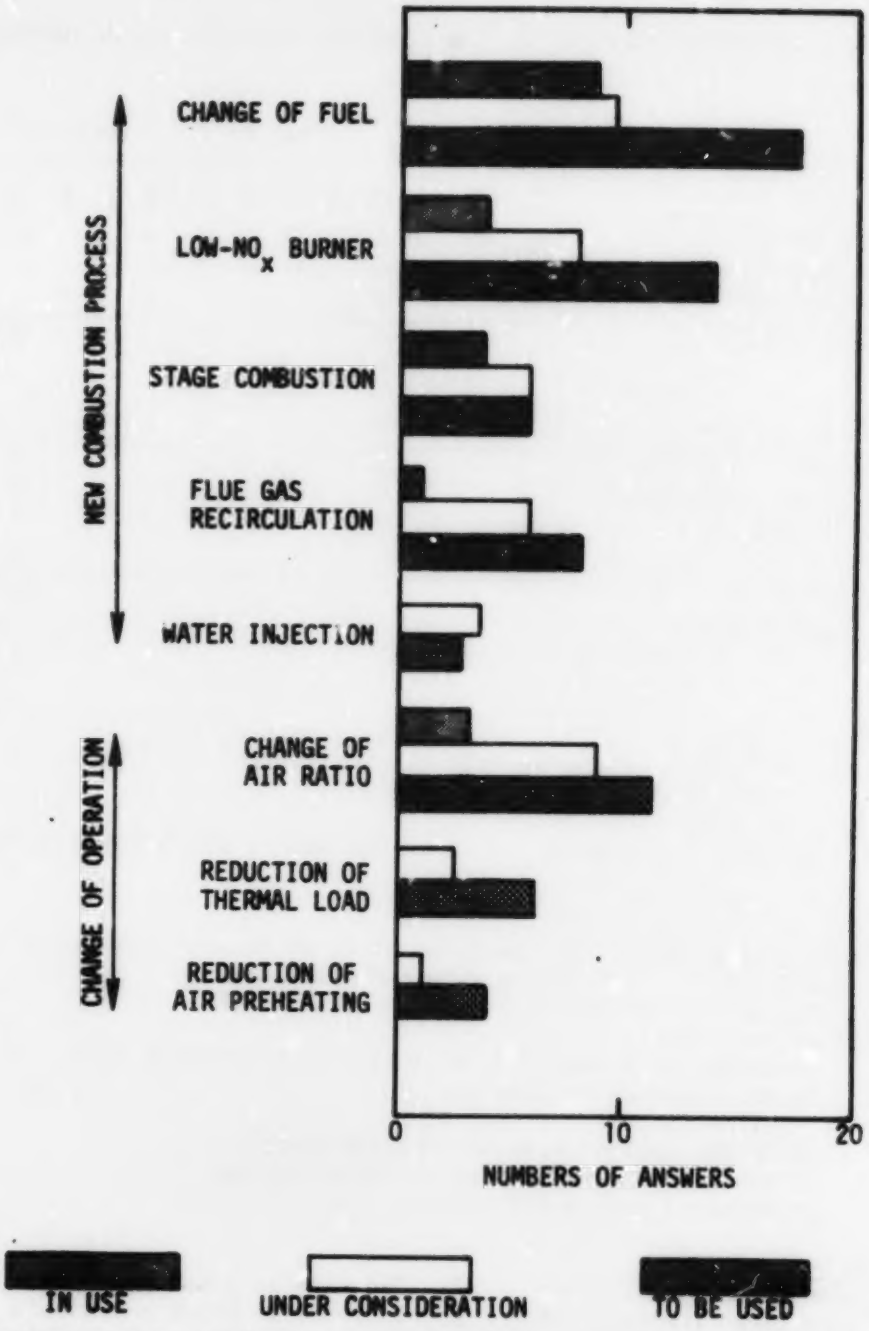


Figure 2-1. Status of combustion control at 114 plants. (Results of opinion survey)

Table 2-2. CHARACTERISTICS OF COMBUSTION MODIFICATION METHODS

	Thermal NO_x				Fuel NO_x				Problems			
	A	B	C	D	E	F	G	H	I	J	K	L
Change of air ratio	◎	◎	◎	△		○	○	◎	△			×
Thermal load reduction	◎	◎	○	△		△	△	◎	○		○	○
Less air preheating	◎		○	○				◎	×		×	
Low-NO_x burner: Good mixing	○		◎	◎				○				◎
Low-NO_x burner: Divided flame	◎		◎	◎				○				
Low-NO_x burner: Self-recirculation	○	◎	○	◎		○		○				
Low-NO_x burner: Stage burning		◎		◎		○		○				
Stage combustion		◎		◎		○	○	△				×
Off-stoichiometric combustion		◎		◎		○	○	○				×
Flue-gas recirculation	◎		○	◎				△	×			×
Water (steam) injection	◎		○	○				○	×			○
Change of fuel	◎	◎	◎	□	○		◎	△				◎
Combustion chamber design	◎		○	◎				△				

Thermal NO_x

A: Temperature drop B: Decrease of O_2 in burning zone
C: Decrease of retention time in high temperature zone
◎ Closely related ○ Related
D: Degree of decrease
◎ Large ○ Small △ Varies with installations □ Not clear

Fuel NO_x

E: Decrease of N in fuel F: Decrease of O_2 in initial combustion zone
○ Effective △ Varies with installations
× Has adverse effect
G: Degree of decrease
◎ Large ○ Small △ Varies with installations
× NO_x increase is possible
H: Ease of application
◎ Easily applied also to existing plants
○ Needs some modification of installations
△ Requires much modification

Problems to be considered

I: Decrease in heat efficiency J: Decrease in power generation
K: Need for large installation L: Increase in other pollutants (dust, CO, hydrocarbons, etc.)
× Closely related △ Related
○ Varies with installations ◎ Possibly improved

the basic design is a single control element configuration, whereby air is injected in a continuous cylindrical stream, which mixes with the jets of fuel injected radially outward through a large number of shaped ports. The air and fuel are then further mixed by means of a deflector, which serves both to complete the mixing process and as a flame holder.

The intermixing of fuel and air produces a radial conical flame pattern that is quite thin. Keeping the flame front thin and flat, provides a maximum radiation surface and allows rapid dissipation of heat from the flame. The shape of the flame front ensures an extremely short nitrogen-oxygen reaction time. Recirculation also reduces combustion temperature. The effect of the burner is shown in Figure 2-3.

State of Development

TRW has supplied burners for oil with capacities ranging from 4,560,000 to 24,100,000 kcal/hr: 11 units in Japan and a few in the United States. A duel type for oil and gas was commercialized in early 1975.

Advantages

The burner reduces not only NO_x but also soot emissions. It requires neither redesign of the boiler nor reduction of load on the boiler combustion chamber. Less steam is consumed, for fuel atomization.

Disadvantages

The device is applicable only to boilers. Pressure drop at burner throat is high.

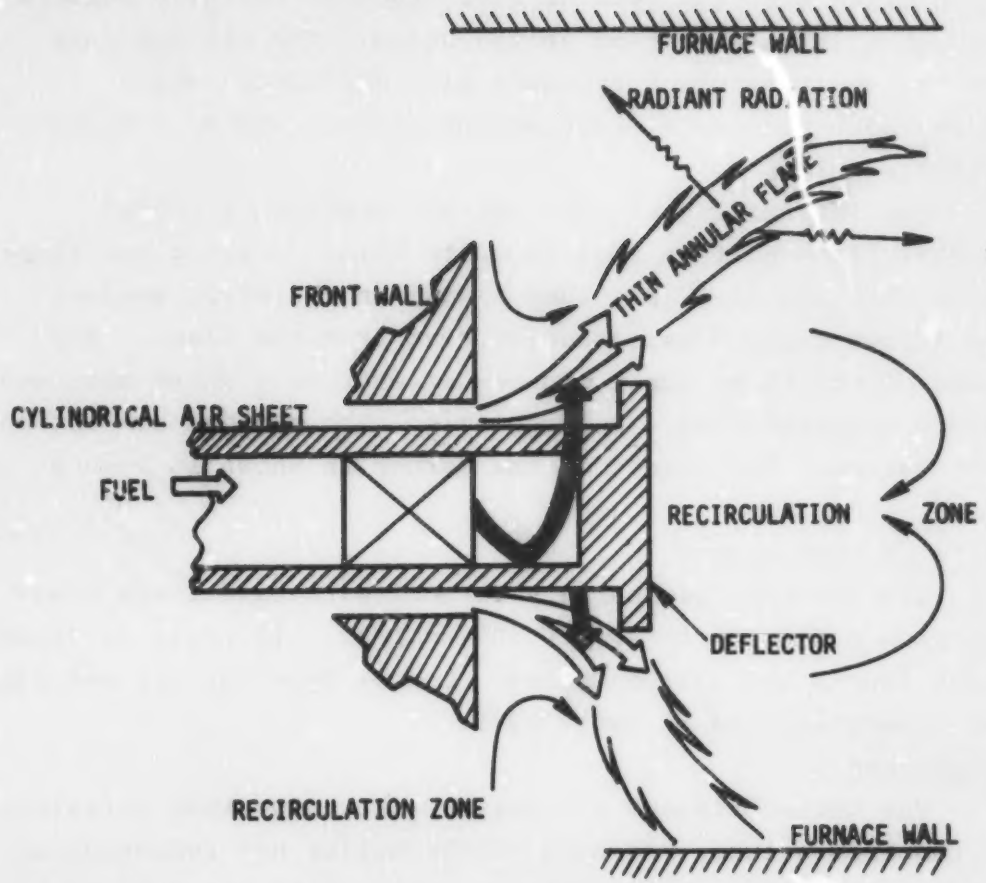


Figure 2-2. NFK-TRW burner.

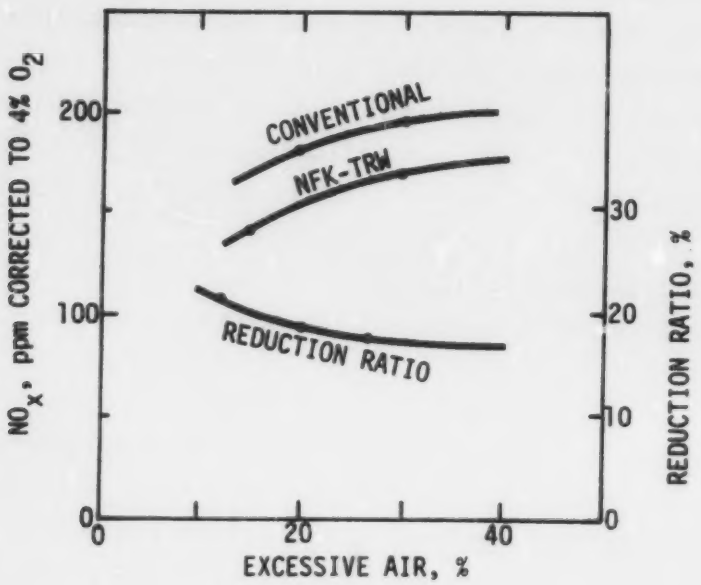


Figure 2-3. Effect of NFK-TRW burner.
(Heavy oil, N = 0.3%, 310 liter/hr)

SRG TYPE BURNER

Description

Configuration of the SRG burner is shown in Figure 2-4.

Without requiring special power, the burner recirculates air and part of the combustion products into the burner tile by the jet energy of fuel and atomizing steam. Because it accomplishes gasification burning of fuel, this burner is called the self recirculating gasification (SRG) burner. The angle of the atomizing nozzle is from 30 to 45 degrees. The effect of the burner is shown in Figure 2-5.

State of Development

Over 1000 natural-draft units have been sold in Japan. Ten recently developed forced-draft units have also been supplied.

Advantages

This burner is applicable to many types of industrial furnaces in oil refining, petrochemical, iron and steel, cement, and other industries. A wide turndown ratio under stable flame conditions is attained. Oil, gas, and oil-gas combination burners are available.

Disadvantages

The flame is shaped like a candle flame, and this shape cannot be altered.

DAIDO STEEL LOW-NO_x BURNER

Background

The developer is Daido Steel Co., a steel producer with a machinery division manufacturing burners and furnaces. Daido has developed a self-recirculation burner under a technical license agreement with Caloric Gesellschaft für Apparate Bau (West Germany).

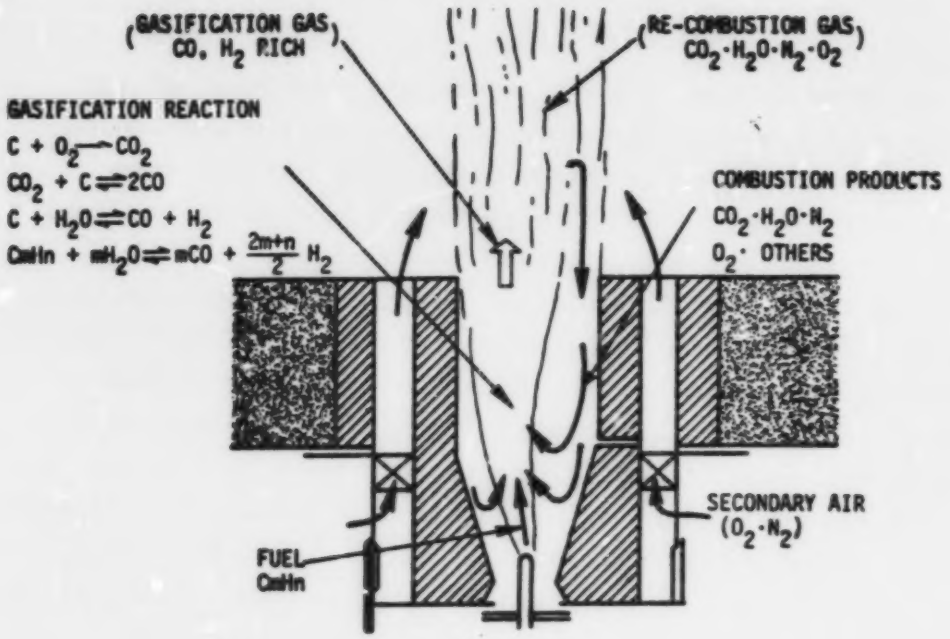


Figure 2-4. Principle of SRG burner.

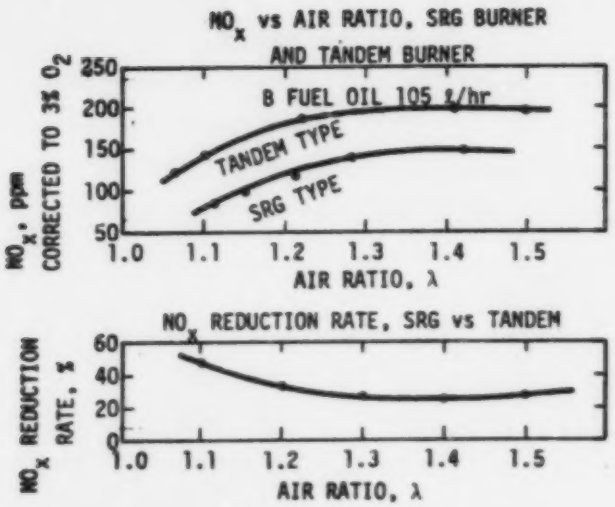


Figure 2-5. Effect of SRG burner.

Description

As shown in Figure 2-6, (A and B), injection of air through a narrow space between the ring nozzle and combustion chamber causes a pressure difference between them. Thus a part of the combustion gas recirculates to the fuel chamber to reduce the combustion temperature.

View (A) shows the original design of Caloric Gesellschaft. Because the high-temperature flue gas with relatively few particulates jets from the combustion chamber, where the combustion is completed, this type of burner is suitable for heat treatment or drying. View (B) is the modified type developed by Daido Steel. Because the flame front is longer, heat dissipation from the flame is more rapid than in the original design and this type of burner is thus more efficient in NO_x reduction. Effects of the burners are shown in Figure 2-7. Part of the fuel injected into the fuel chamber by oil pressure, steam, or air reacts with the recirculating hot gas to form intermediates such as aldehydes and alkyl radicals, which are rapidly oxidized by air from the ring nozzle.

Several units have been used for heating furnaces in the nonferrous metal refining industry. This type of burner can also be used for submerged combustion. Design and tests of units of various sizes from 10^5 to 5×10^6 kcal/hr have been completed. A field test of the application to a heating furnace for the iron and steel industry is being planned.

Price and Operation Cost

Examples of price (December 1974) are as follows:

1 million kcal/hr	$4,500
4 million kcal/hr	$13,000

Operating costs are slightly higher than for ordinary

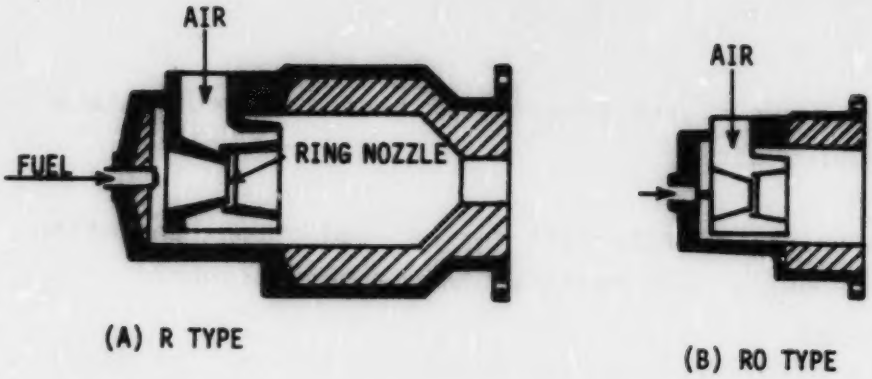


Figure 2-6. Daido Steel low-NO_x burners.

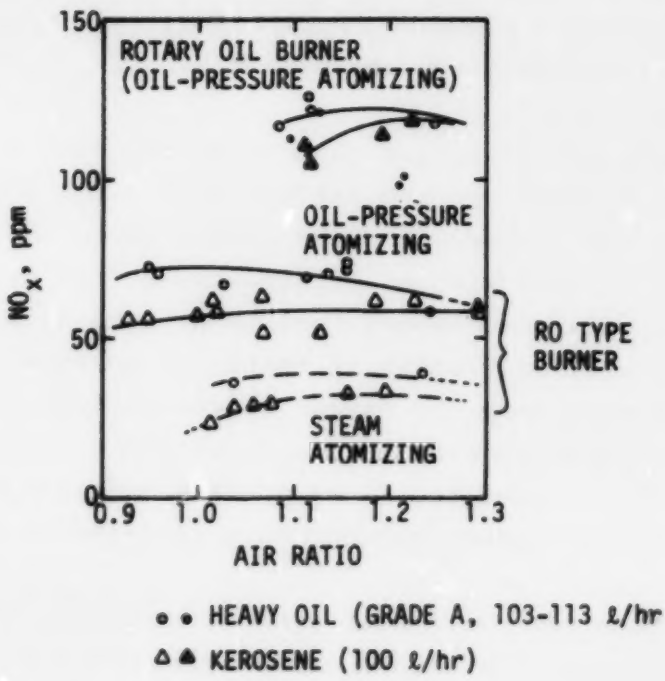


Figure 2-7. Effect of RO type burner.

burners, because higher pressure is needed to recirculate the combustion air.

Advantages

This burner is effective for NO_x reduction; formation of carbon monoxide and particulates is very slight.

Disadvantages

Large-size units of over 5 million kcal/hr are difficult to construct. Residual oil cannot be used.

MHI SLIT BURNER

Background

The developer is Mitsubishi Heavy Industries Co. (MHI). MHI is the largest heavy manufacturer in Japan, turning out a wide variety of products including ships and boilers. MHI recently developed a low-NO_x burner that is a kind of off-stoichiometric combustion gas burner.

Description[3]

The basic structure of the burner is shown in Figure 2-8. Premixed fuel gas and air are fed to the combustion chamber in three layers. In the middle layer the gas is enriched, i.e. fuel with an off-stoichiometric quantity of air; in the outer two layers fuel is diluted with excess air. The overall air ratio is nearly 1, so that combustion takes place at a very low oxygen concentration. Moreover, this special type of atomizer is designed to produce a thin film flame to enlarge the flame surface and thus reduce NO_x emission through flame cooling and a self-recirculation effect.

Test furnaces, with heat generating rates of 4×10^6 and 2.8×10^7 kcal/hr were operated with propane and methane as fuels to study the effects of the burner. Some of the results are shown in Figure 2-9. Application to liquid

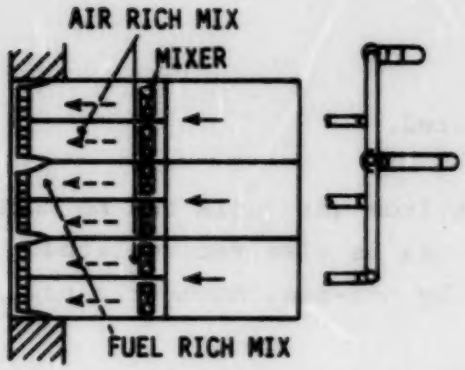


Figure 2-8. Model of MHI low-NO_x burner.

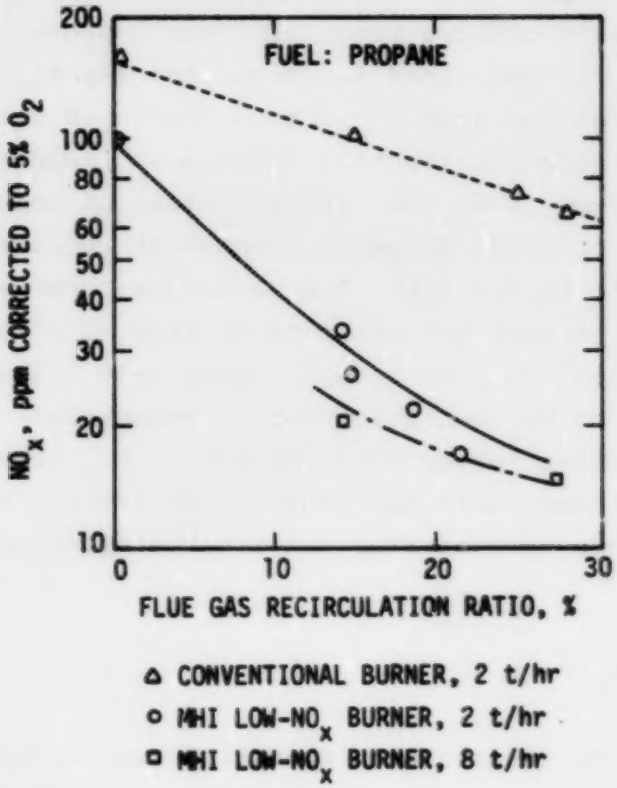


Figure 2-9. Effect of MHI low-NO_x burner.

fuels is being tested.

Advantages

NO_x emissions from gas fuels can be substantially reduced when flue gas is also recirculated. Fuel NO_x may also be decreased by off-stoichiometric combustion.

Disadvantages

The MHI burner is applicable only to limited types of industrial furnaces.

IHI DIVIDED-FLAME BURNER

Description

The developer is Ishikawajima-Harima Heavy Industries Ltd. (IHI), one of Japan's leading heavy manufacturers working also on boiler construction. IHI has improved its divided-flame burners, described in an earlier report,[1] and has developed several new ones.[4] Burners developed for power up to 600 MW gave satisfactory results in field tests. This type of burner might be the cheapest means of reducing NO_x emissions from existing boilers, because it requires simply replacing the burner tip. The reduction, however, does not exceed 40 percent for existing boilers although it could reach 50 percent for new ones. Figure 2-10 illustrates the results of NO_x reduction for 16 commercial boilers with capacities larger than 200 t/hr. NO_x reduction by this burner decreases with the increase of effects of other control methods such as flue gas recirculation and staged combustion.

RESEARCH ON FUEL NO_x[12]

Background

Central Research Institute of Electric Power Industry (CRIEP) has made extensive tests on combustion modification.

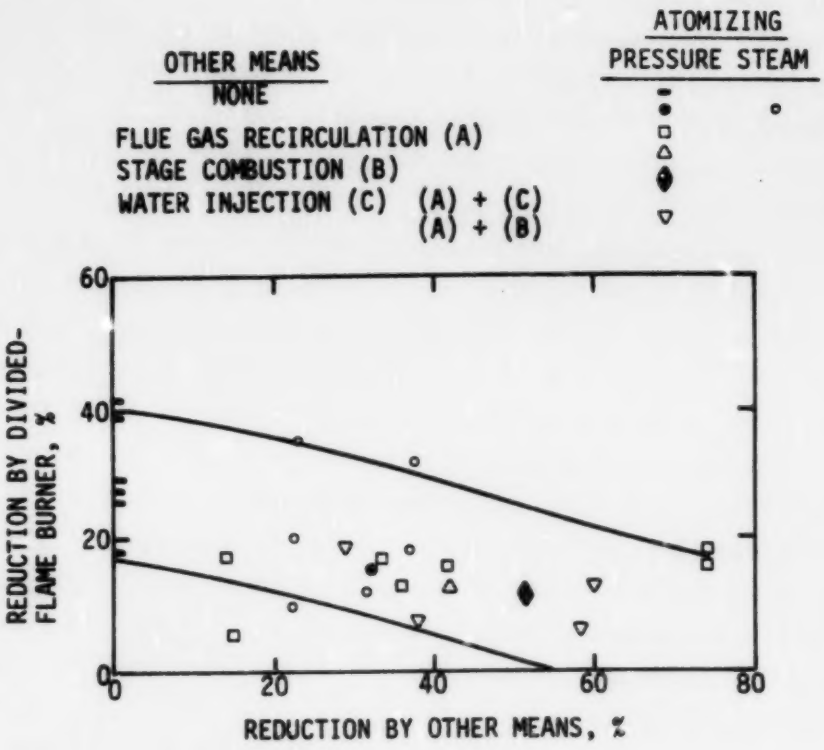


Figure 2-10. NO_x reduction by IHI burner and other means.

Some of the results of tests on fuel NO_x are discussed below.

Experimental Furnace

Fuel flow rate: 50 liters/hr

Burner: pressure-atomizing type (steam or air)

Heat generating rate: 2.48×10^5 kcal/m^3 hr

Maximum air preheat temperature: 350°C

Maximum fuel preheat temperature: 150°C

Experimental Results

Figure 2-11 shows the correlation between NO_x concentration (corrected to 4% O_2) and the amount of bound nitrogen in fuel oil. Various amounts of quinoline were added to grade C heavy oil (N = 0.2%) to vary the nitrogen content in the fuel. NO_x concentration increased linearly with N content. Figure 2-12 shows that conversion of the bound nitrogen to NO_x was strongly dependent on O_2 concentration and was independent of the amount of N in the fuel. Figures 2-13 and 2-14 show similar results of field tests carried out at a 125-MW power plant. As shown in Figure 2-15 there were some differences of conversion ratio in tests of the different-sized units.

Figure 2-16 shows the flame-temperature dependence of the conversion ratio.

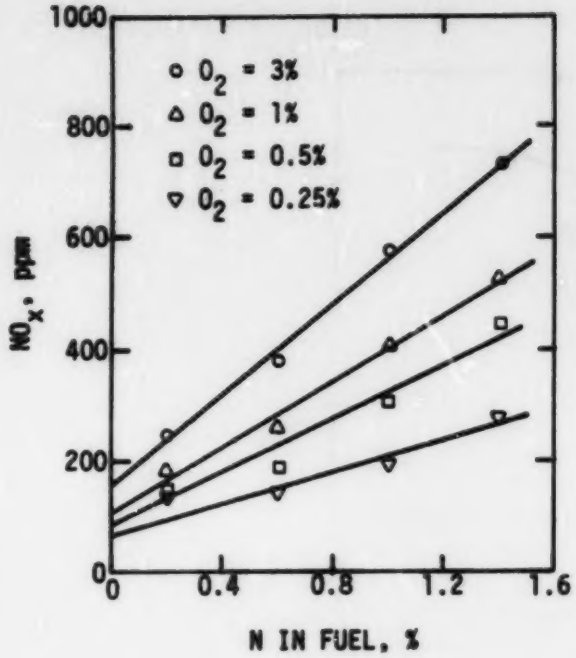


Figure 2-11. Results at test furnace.

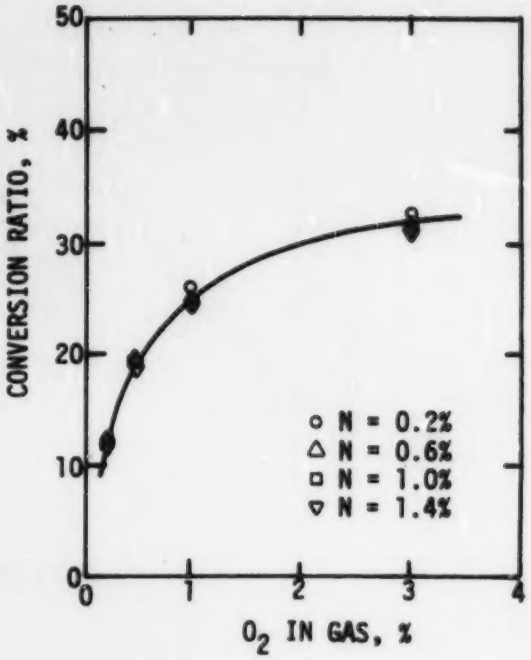


Figure 2-12. Results at test furnace.

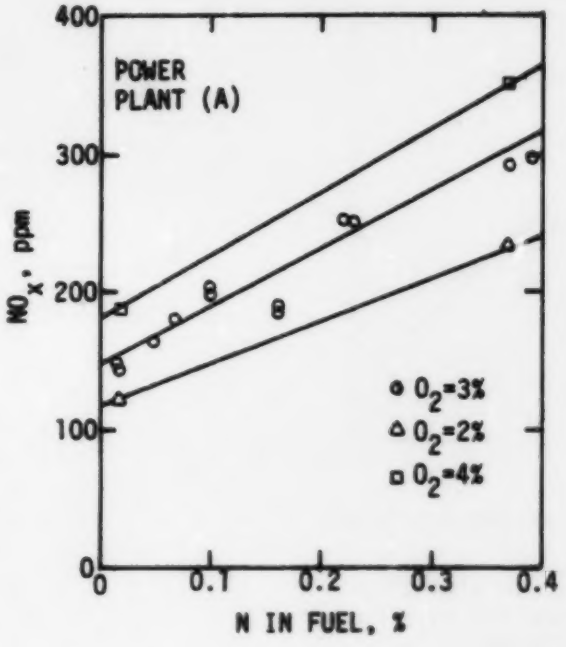


Figure 2-13. Results at 125-MW power plant.

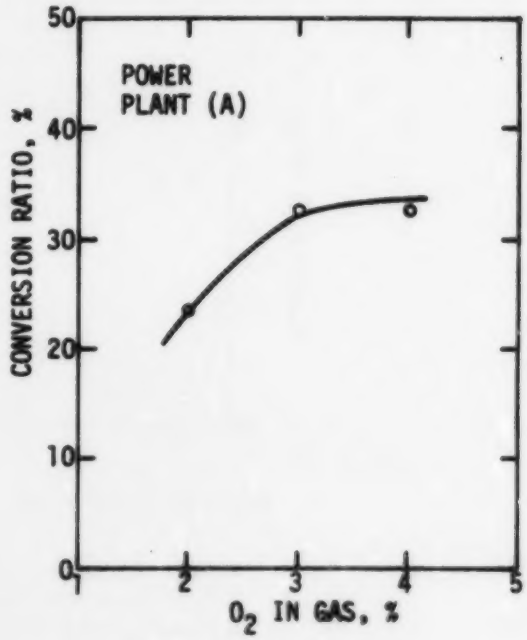


Figure 2-14. Results at 125-MW power plant.

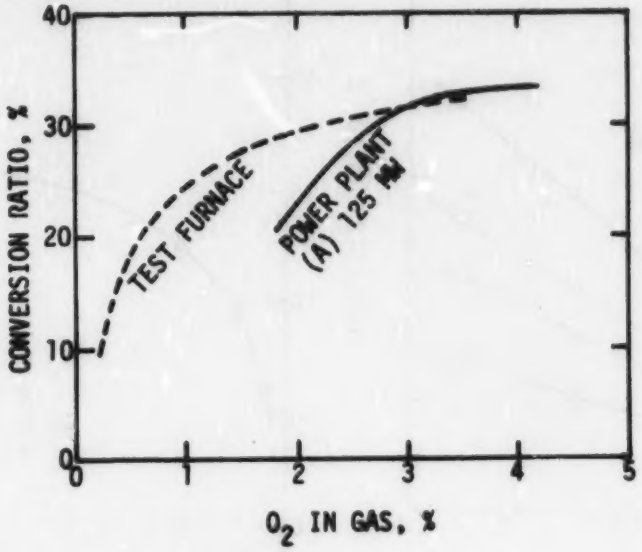


Figure 2-15. Comparison of conversion ratio at power plant and test furnace.

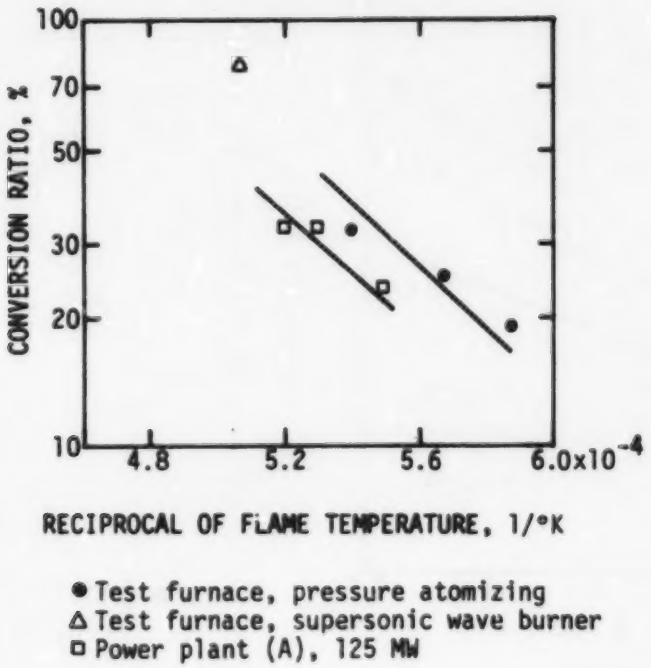


Figure 2-16. Flame temperature and conversion ratio.

3. NO_x REMOVAL BY WET PROCESSES

GENERAL DESCRIPTION

Major Wet Processes and Plants for NO_x Removal

In Japan, sodium scrubbing has been used to remove NO_x from NO_x-rich gases produced in relatively small amounts at metal-dissolving plants, nitric acid plants, etc. The by-product solution containing sodium nitrate and nitrite is purged after dilution except in nitric acid plants, which recover them for limited use. In treating large amounts of flue gas, neither purging nor recovery is acceptable. In recent years, many wet processes for NO_x removal have been developed with the aim of eliminating troublesome by-products or removing NO_x and SO_x simultaneously. Major processes and plants are listed in Table 3-1.

Most of the NO_x in flue gas is present in the form of NO, which is inactive and not easily absorbed by liquors. NO is usually oxidized into NO_2 or N_2O_5, which are much more easily absorbed. For the oxidation, ozone is used in the Chiyoda and Tokyo Electric-Mitsubishi H.I. processes; chlorine dioxide, ClO_2, in the Sumitomo-Fuji Kasui process; sodium or potassium permanganate in the Nissan and MON processes; and calcium hypochlorite, $Ca(OCl)_2$, in the Kobe Steel process. In the Ube and Kawasaki processes, NO_2 is added to the gas to maintain the NO_2/NO mole ratio at 1 to promote the absorption.

In the processes being developed by the Central Research Laboratory of Electric Power Industry (CRIEP),

Table 3-1. MAJOR PLANTS FOR NO_x REMOVAL FROM FLUE GAS BY WET PROCESS

Process developer	Type of process	Plant owner	Plant site	Capacity, Nm^3/hr	Source of gas	Completion	By-product
Sumitomo Metal Fuji Kasui	Redox	Sumitomo Metal	Amagasaki	62,000	Boiler[a]	December 73	$NaNO_3$, NaCl Na_2SO_4
Sumitomo Metal Fuji Kasui	Redox	Toshin Steel	Fuji	100,000	Furnace[d]	December 74	$NaNO_3$, NaCl Na_2SO_4
Sumitomo Metal Fuji Kasui	Redox	Toshin Steel	Osaka	39,000	Boiler[a]	December 74	$NaNO_3$, NaCl Na_2SO_4
Chiyoda	Redox	Chiyoda	Kawasaki	1,000	Boiler[a]	1973	Gypsum $Ca(NO_3)_2$
Tokyo Electric Mitsubishi H.I.	Oxidation absorption	Tokyo Electric	Minami-Yokohama	2,000	Boiler[b]	December 73	HNO_3
Tokyo Electric Mitsubishi H.I.	Oxidation absorption	Tokyo Electric	Minami-Yokohama	100,000	Boiler[b]	October 74	HNO_3
Mitsubishi Metal MKK, Nihon Chem.	Absorption oxidation	Mitsubishi Metal	Omiya	4,000	Boiler[a]	December 74	HNO_3
Fed. of Electric Power Ind. Kureha Chemical	Reduction	Kureha Chem.	Nishiki	5,000	Boiler[a]	April 75	Na_2SO_4 N_2
Fed. of Electric Power Ind. Kawasaki H.I.	Magnesium scrubbing	EPDC	Takehara	5,000	Boiler[c]	December 75	Gypsum $Ca(NO_3)_2$
Kobe Steel	Redox	Kobe Steel	Kakogawa	1,000	Furnace[e]	December 73	Gypsum N_2
Chisso Corp.	Reduction	Chisso Pet. Chem.	Goi	300	Boiler[a]	1974	$(NH_4)_2SO_4$

[a] Oil-fired boiler.

[b] Gas-fired boiler.

[c] Coal-fired boiler.

[d] Metal heating furnace

[e] Iron ore sintering furnace.

Kureha, and Chisso, NO is absorbed without oxidation under the presence of a catalyst.

Various kinds of by-products are produced: nitric acid by the Tokyo Electric-Mitsubishi H.I. process, potassium nitrate by the MON process, ammonium sulfate by the Chisso process, and calcium nitrate by the Kawasaki process. CRIEP and Kureha intend to reduce NO into N_2. In the Sumitomo-Fuji Kasui and Chiyoda processes, a portion of NO_x is converted into N_2 and the rest into nitrate.

NO Oxidizing Agents

Oxidation of NO in the gas phase by ozone or chlorine dioxide occurs much more rapidly than oxidation in the liquid phase by permanganates or hypochlorites; although permanganates and hypochlorites are strong oxidizing agents, absorption of NO in the liquid phase is slow.

Ozone produced from air by an electrically driven ozone generator is capable of oxidizing NO not only to NO_2 but also to N_2O_5, which readily reacts with water or alkaline solutions to form nitric acid or nitrates. Ozone, however, is fairly expensive.

Converting the NO in flue gas from a 35-MW oil-fired boiler into NO_2 requires 400 to 600 kg/hr of ozone, assuming that the gas contains 200 to 300 ppm NO. Figure 3-1 shows a rough estimation of the capital costs for ozone generation. Power consumption by an ozone generator is assumed to be approximately 32 kWh per kilogram of ozone; the cost of ozone calculated from the capital and power consumption is roughly 1.3 to $1.5 per kilogram or 2.7 to $3.0 per cubic meter; these values indicate that ozone costs 500 to $900 per hour for the 35-MW plant or 7 to $12 per kiloliter of oil. Because of the high cost of ozone, therefore, NO concentration in flue gas should be kept low by combustion

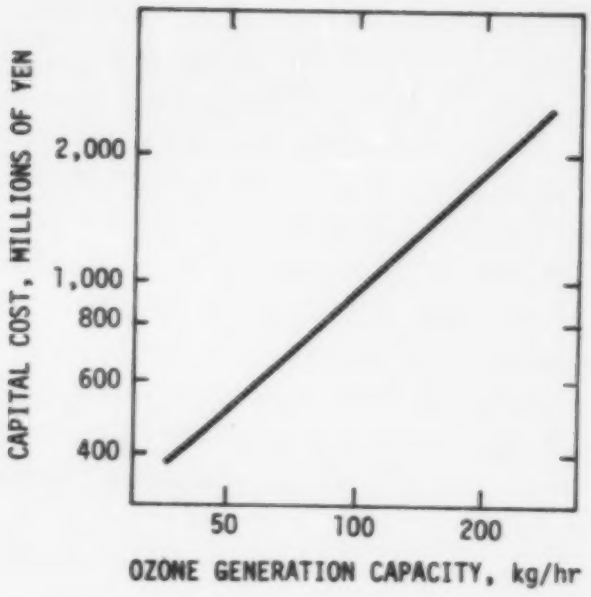


Figure 3-1. Capital cost for ozone plant.[5]

control to reduce ozone consumption.

Chlorine dioxide is also an effective oxidizing agent but it adds a chloride to the by-product and complicates the treatment.

Reaction of NO_x with Liquids

When NO and NO_2 are present at high equal concentrations, a substantial amount of N_2O_3 is formed, which is readily absorbed by an alkaline solution to form a nitrate.

$$NO + NO_2 = N_2O_3 \quad (1)$$

$$2NaOH + N_2O_3 = 2NaNO_2 + H_2O \quad (2)$$

When NO_x concentration is low, as in ordinary flue gas, N_2O_3 does not form in significant amounts even when the NO/NO_2 mole ratio is 1 and the absorption rate is low.

The reaction rate of NO_2 with NaOH or water is much lower than that of SO_2 with NaOH, as shown in Figure 3-2. NO_2 reacts fairly rapidly with sodium and ammonium sulfites.

The reaction of NO_2 with sulfites forms nitrites, N_2, and a small amount of N_2O. Although the reaction mechanisms are not clear, the main reactions may be described simply as follows:

$$3SO_3^{--} + 2NO_2 + H_2O = 2NO_2^{--} + 2HSO_3^{-} + SO_4^{--} \quad (3)$$

$$4SO_3^{--} + 2NO_2 = 4SO_4^{--} + N_2 \quad (4)$$

Reaction (4) is predominant when a large excess of sulfite ion is present. Because alkali scrubbing of flue gas containing SO_2 produces the sulfite ion, these reactions are useful in the simultaneous removal of SO_2 and NO_x.

NO hardly reacts even with sulfite solutions. Use of a catalyst, however, can promote the reaction. CRIEP and Kureha use a catalyst to absorb NO and to convert it into N_2. Chisso uses a different kind of catalyst to reduce most of the NO into NH_3.

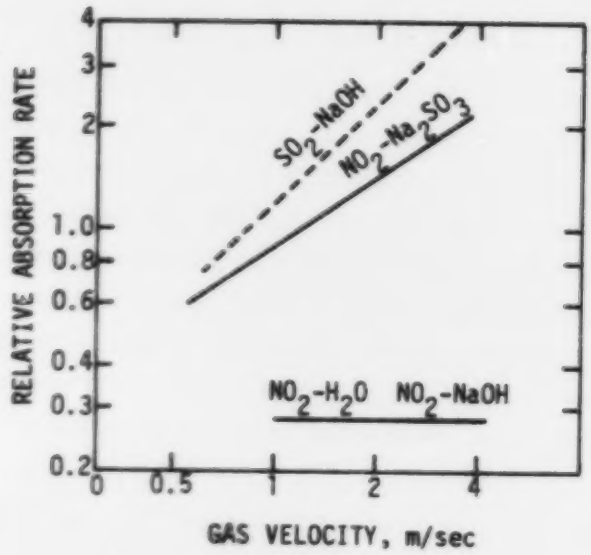


Figure 3-2. Relative absorption rate in various systems (NO_x 200-1,000 ppm).[6]

Concentrated sulfuric acid can absorb NO and NO_2, but the reaction is not useful in flue gas treatment because of the low reaction rate and the presence of much moisture in flue gas.

Advantages and Disadvantages of Wet Processes

The advantages of the wet process over the dry process (catalytic reduction) are as follows:

(1) Simultaneous removal of SO_2 and NO_x is possible.

(2) Heating the gas to a high temperature (such as to 350 to 400°C in selective catalytic reduction) is not necessary.

(3) The process is not disturbed seriously by dust as in catalytic reduction.

(4) Although a wet process may be expensive, it may by-produce a fertilizer such as potassium nitrate or ammonium sulfate, whereas in selective catalytic reduction a large amount of ammonia is converted into N_2.

Wet processes have the following disadvantages :

(1) Most processes use an expensive oxidizing agent.

(2) NO_2 reacts much more rapidly than NO but still much more slowly than SO_2. A large absorber is required.

(3) Concentration of the absorbing liquor, normally dilute, uses much energy to recover useful by-products.

(4) Demand for the by-products is limited.

(5) Liquors containing nitrate or nitrite should not be purged. Removing these compounds from wastewater is difficult.

Generally, although wet processes are advantageous for removal of SO_2, they may be more troublesome than dry processes for removal of NO_x.

SUMITOMO-FUJI KASUI PROCESS (MORETANA PROCESS)

Background

The process developers are Sumitomo Metal Industries Ltd. and Fuji Kasui Kogyo K. K. Sumitomo Metal is a large steel producer, and Fuji Kasui is an engineering firm concerned primarily with wastewater treatment. They have jointly developed a process for simultanecus removal of SO_2 and NO_x. A semicommercial plant with a capacity of treating 62,000 Nm^3/hr of flue gas from an oil-fired boiler was completed in 1973 at the Amagasaki Works, Sumitomo Metal. Two commercial plants of relatively small size went into operation recently (Table 3-1).

Process Description

A flowsheet of the process is shown in Figure 3-3. Flue gas is first cooled to 55 to 65°C in a cooler by a water spray. An oxidizing agent, gaseous chlorine dioxide, ClO_2, is added to the gas just before the scrubber; it oxidizes NO into NO_2 within 0.5 second. The gas is then introduced into a "Moretana scrubber" with four stages of perforated plates, which provide excellent gas-liquid mass transfer. In reaction of the gas with a sodium hydroxide-sulfite solution, more than 98 percent of the SO_2 is absorbed to produce sodium sulfite, which reduces NO_2 into N_2. The main reactions involved are as follows:

$$2NO(g) + ClO_2(g) + H_2O = NO_2(g) + HCl(g) + HNO_3(g)$$

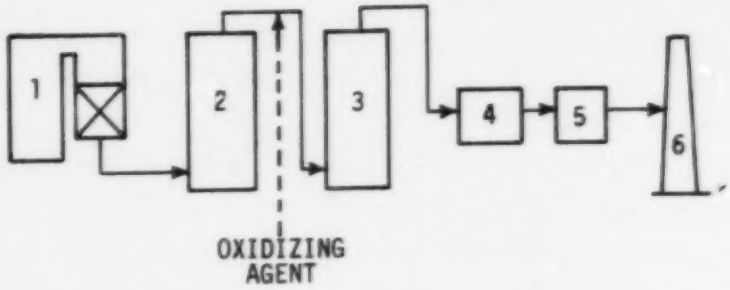
$$HCl(g) + NaOH(aq) = NaCl(aq) + H_2O$$

$$HNO_3(g) + NaOH(aq) = NaNO_3(aq) + H_2O$$

$$SO_2(g) + 2NaOH(aq) = Na_2SO_3(aq) + H_2O$$

$$2NO_2(g) + 4Na_2SO_3(aq) = N_2 + 4Na_2SO_4(aq)$$

The use of stoichiometric amounts of ClO_2 eliminates about 90 percent of the NO_x in the gas. About half of the



1: BOILER 2: COOLER
3: SCRUBBER 4: MIST ELIMINATOR
5: AFTER BURNER 6: STACK

Figure 3-3. Flowsheet of Sumitomo - Fuji Kasui process.

removed NO_x is converted into N_2 and the rest into sodium nitrate. A large excess of Na_2SO_3 is required for the formation of N_2. The ClO_2 is produced by reacting $NaClO_3$ with concentrated SO_2 and H_2SO_4.

$$Na_2SO_3 + 2H_2SO_4 = SO_2 + 2NaHSO_4$$

$$2NaClO_3 + SO_2 + H_2SO_4 = ClO_2 + 2NaHSO_4$$

When the flue gas contains 260 ppm NO_x, mainly in the form of NO, 1500 ppm SO_2 in flue gas derived from 3 percent sulfur oil is not sufficient for the reactions and a small amount of make-up $NaSO_3$ is needed. The lower the concentration of SO_2 in the flue gas, the larger the required amount of make-up $NaSO_3$.

The by-product of the scrubbing, a solution containing NaCl, Na_2SO_4, and $NaNO_3$, is purged after dilution. Studies are being directed toward recovering NaCl from the solution and producing $NaClO_3$ or at recovering Na_2SO_4 and producing NaOH and H_2SO_4 by electrolysis.

Tests on ammonia scrubbing at a 25,000 Nm^3/hr pilot plant are planned with a view to by-producing gypsum and ammonia compounds for use in fertilizers.

Evaluation

Capital cost is in the range of 60 to $90 per kilowatt. Operating cost including depreciation (7 years) is estimated roughly at $30 per kiloliter of oil or 7 mills per kWh without wastewater treatment.

The scrubbing process is simple and the removal ratio is high for both SO_x and NO_x. A major drawback of the process is the by-production of liquor containing NaCl, Na_2SO_4, and $NaNO_3$, which is difficult to treat. Use of ozone in place of ClO_2 is considered. When ozone is used, the by-product liquor contains no NaCl but is still not easy

to treat. Moreover, ozone is costlier than ClO_2. Application of the process on a large scale may not be feasible unless the liquor can be adequately treated.

Ammonia scrubbing may be a good way to eliminate production of the troublesome sodium salts and to recover useful by-products. The process may create a plume, however. Moreover, the by-product, a mixture of ammonium nitrate, chloride, and sulfate, is very hygroscopic and may not be suited for use in solid fertilizer.

TOKYO ELECTRIC - MITSUBISHI H.I. PROCESS

Background

The process developers are Tokyo Electric Power Co. and Mitsubishi Heavy Industries. Tokyo Electric Power, one of Japan's nine major power companies, and Mitsubishi Heavy Industries, one of the largest ship and machine producers in Japan, jointly introduced a nitric acid by-producing process from U.S.S.R. and constructed at the Minamiyokohama power station of Tokyo Electric Power a pilot plant with a capacity of treating 2000 Nm^3/hr of flue gas from a natural-gas-fired boiler. The plant was operated from December 1973 to September 1974. A larger pilot plant (100,000 Nm^3/hr) went into operation in December 1974 at the same power station.

Process Description

A flowsheet of the smaller test unit is shown in Figure 3-4. The flue gas from the boiler is cooled, injected with ozone, and introduced into an oxidizing tower, where NO_x is oxidized to N_2O_5. The gas is then treated with water in an absorber to produce nitric acid of 8 to 10 percent concentration, which is concentrated to 60 percent for industrial use.

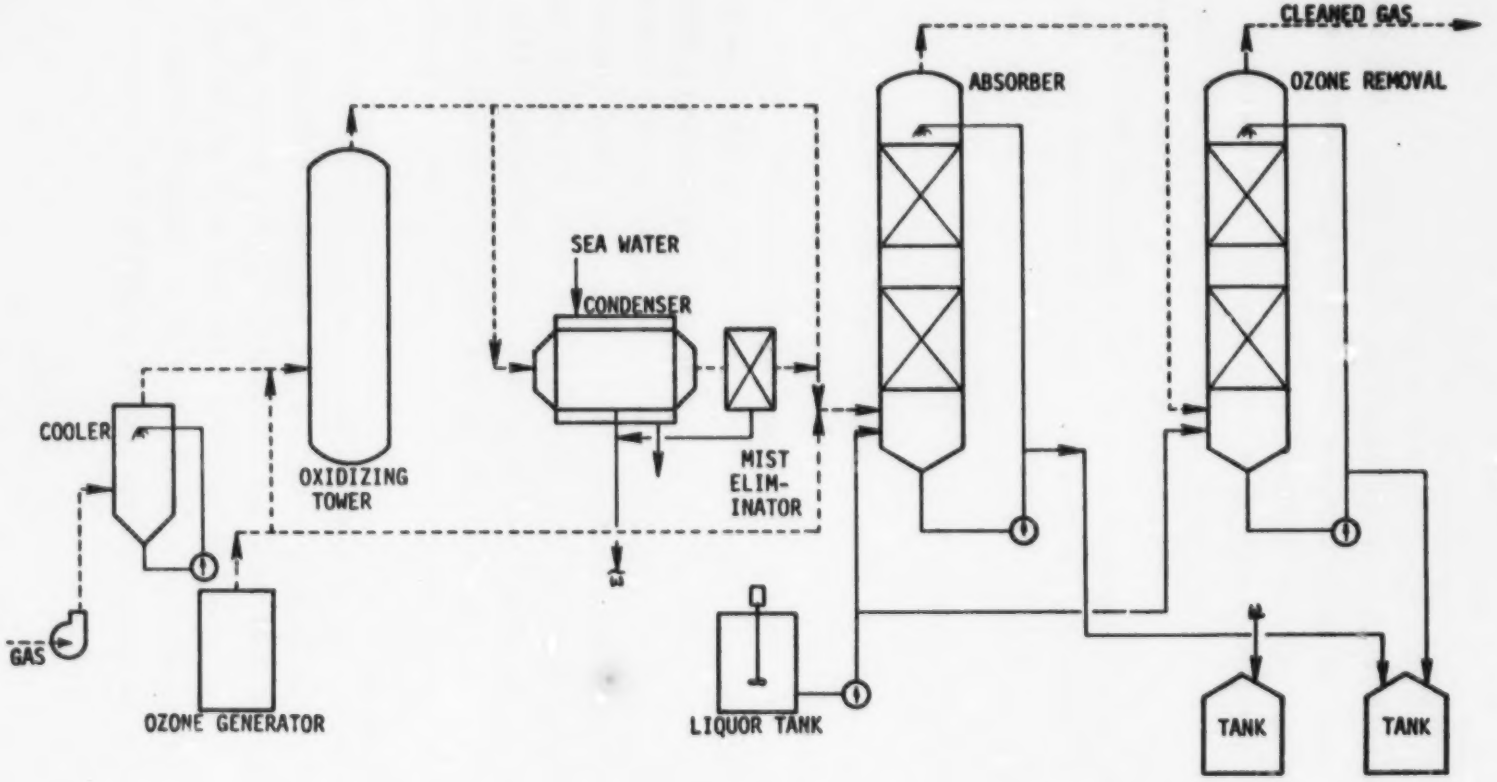


Figure 3-4. Flowsheet of Tokyo Electric - Mitsubishi H. I. process.

$$NO + O_3 = NO_2 + O_2$$

$$2NO_2 + O_3 = N_2O_5 + O_2$$

$$N_2O_5 + H_2O = 2HNO_3$$

As an alternative, the gas discharged from the oxidizing tower is indirectly cooled by sea water, where moisture in the gas condenses and reacts with N_2O_5 to produce dilute nitric acid of about 1 percent concentration. The dilute acid may be decomposed into N_2 and H_2O by biological treatment.

The effluent gas from the absorber or the condenser contains a small amount of ozone. This effluent is treated in an ozone removal tower with a reducing agent such as sodium or calcium sulfite.

$$O_3 + Na_2SO_3 = Na_2SO_4 + O_2$$

$$O_3 + CaSO_3 + 2H_2O = CaSO_4 \cdot 2H_2O + O_2$$

Performance

The smaller test unit was operated for about 9 months. The gas contained 90 to 220 ppm NO_x, 8.5 percent CO_2, 16.8 percent H_2O, and 2.6 percent O_2.

The NO_x removal ratio was kept over 90 percent by control of oxidation temperature, O_3/NO_x ratio, and oxidation time. Ozone was almost entirely removed by the ozone removal tower. The recovered nitric acid concentrated to 60 percent was pure enough to meet the relevant Japanese Industrial Standard. In some tests, NO was oxidized into NO_2 with ozone (no oxidizing tower was needed in this case) and treated with a sodium sulfite solution. More than 90 percent of the NO_2 was removed through the following reaction:

$$2NO_2 + 3Na_2SO_3 + H_2O = 2NaNO_2 + 2NaHSO_3 + Na_2SO_4$$

Process flow at the larger pilot plant (100,000 Nm^3/hr) is similar to that shown in Figure 3-4. The plant has used calcium sulfite for ozone removal and to by-produce gypsum. No operation data have been disclosed.

Evaluation

The process is simple and suitable for treatment of "clean gas" without SO_2. High NO_x removal is achieved without production of waste liquor. On the other hand, the use of ozone and the concentration of nitric acid are costly. Moreover, the demand for nitric acid is limited. The process might be more expensive than a selective catalytic reduction process.

CHIYODA THOROUGHBRED 102 PROCESS[5]

Background

The process developer is Chiyoda Chemical Engineering and Construction Co. Chiyoda has developed an SO_2 removal process called Thoroughbred 101 and has constructed many commercial plants. The process designated 102 entails a simple addition of an ozone injection step to the 101 process for simultaneous removal of NO_x and SO_2. A pilot plant (1000 Nm^3/hr flue gas from an oil-fired boiler) has been in operation.

Process Description

A flowsheet of the process is shown in Figure 3-5. Flue gas is cooled in a cooler to 50 to 60°C, injected with ozone and air to oxidize NO into NO_2, and then introduced into a packed tower scrubber and treated with dilute sulfuric acid containing a ferric iron catalyst. More than 60 percent of the NO_x and 90 percent of the SO_2 are removed (Figure 3-6). A portion of the removed NO_x forms nitric acid and the rest forms N_2 and N_2O, both of which are harm-

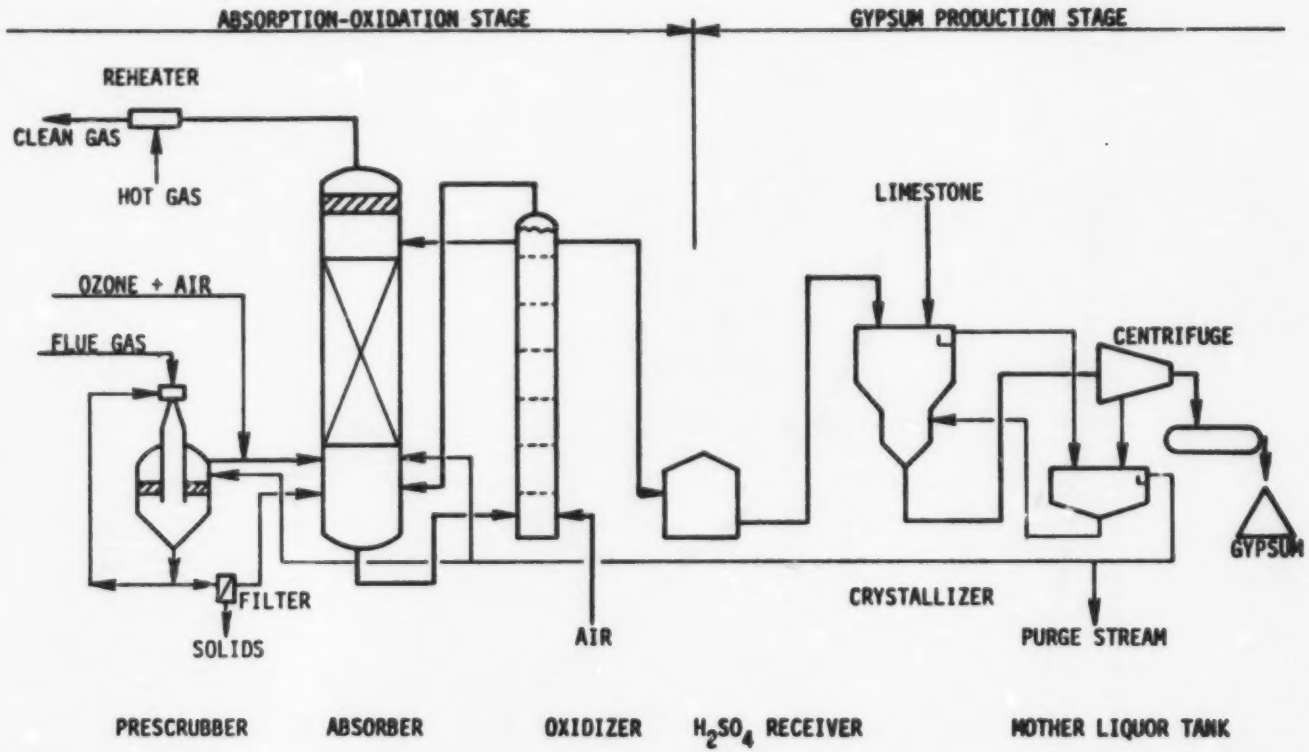


Figure 3-5. Flowsheet of Chiyoda Thoroughbred 102 process.

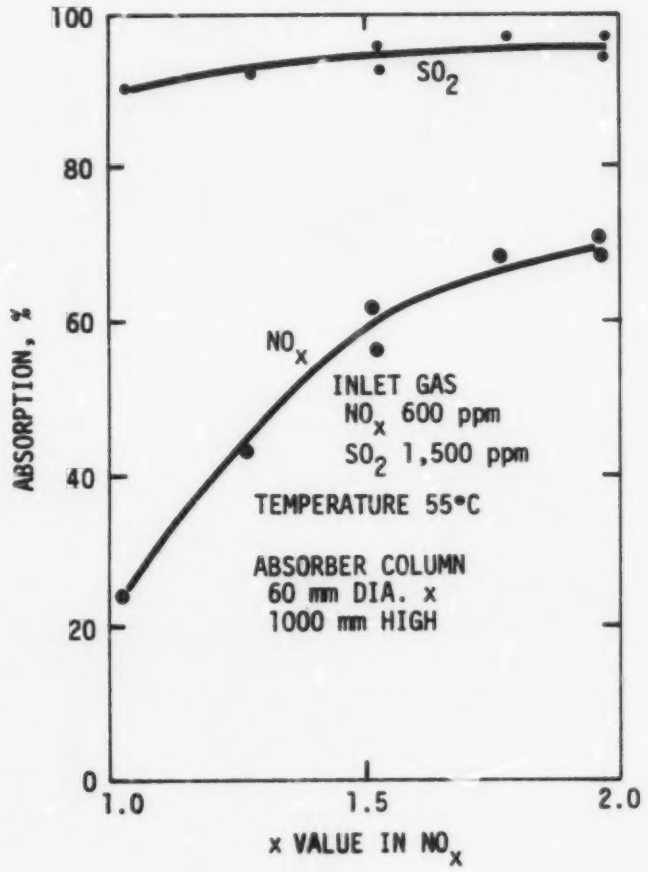


Figure 3-6. Relation between oxidation ratio and removal of SO_2 and NO_x.

less gases. The liquor discharged from the scrubber is oxidized by air bubbles to convert SO_3^{--} into SO_4^{--} and Fe^{++} into Fe^{+++}. Most of the liquor is returned to the scrubber; a portion is reacted with powdered limestone to precipitate gypsum. The gypsum slurry is centrifuged. A portion of the mother liquor is purged to prevent the accumulation of nitric acid and impurities derived from flue gas and limestone.

Evaluation

The process is simple and plant operation easy. The NO_x removal ratio is not very high but is acceptable. The major drawback of the process is that wastewater containing calcium nitrate is purged. For application on a large scale, wastewater treatment for denitrification will be needed but may not be easy. Another disadvantage is that the process uses ozone, which is expensive. NO_x concentration of the flue gas should be kept low by combustion control in order to reduce ozone consumption.

NISSAN PERMANGANATE PROCESS[7]

Background

The process developer, Nissan Engineering, Ltd., is a subsidiary of Nissan Chemical Industries. Nissan has developed an NO_x removal process using a potassium or sodium permanganate solution and has constructed four small commercial units to treat waste gases from plants using nitric acid, as shown below.

Capacity, Nm^3/hr	Completion
2000	October 1972
100	August 1973
1800	August 1973
1500	March 1975

Process Description

A flowsheet of the process is shown in Figure 3-7. Waste gas rich in NO_x is first washed with an alkali solution to decrease the concentration to 200 to 500 ppm. (This treatment is not needed when NO_x concentration in the gas is less than 500 ppm). The gas is then treated with an alkaline solution containing a permanganate to reduce NO_x to below 50 ppm. The following reactions occur when potassium compounds are used:

Reactions in alkaline solution:

$$NO + KMnO_4 + 2KOH = K_2MnO_4 + KNO_2 + H_2O$$

$$3NO + KMnO_4 + 2KOH = MnO_2 + 3KNO_2 + H_2O$$

$$NO_2 + K_2MnO_4 = KMnO_4 + KNO_2$$

Main reaction in neutral solution:

$$NO + KMnO_4 = MnO_2 + KNO_3$$

The resulting MnO_2 is separated and reacted with KOH to produce K_2MnO_4 by the following reaction:

$$MnO_2 + 2KOH + 1/2\ O_2 = K_2MnO_4 + H_2O$$

K_2MnO_4 is subjected to electrolytic oxidation to regenerate $KMnO_4$. About 0.6 to 1.0 kWh/gram mole K_2MnO_4 is required for the electrolysis.

$$K_2MnO_4 + H_2O = KMnO_4 + KOH + 1/2\ H_2$$

KNO_2 obtained by the reaction in an alkaline solution is treated with sulfuric acid to release concentrated NO, which may be returned to a nitric acid plant. KNO_3 obtained by using a neutral solution can be treated by electrolysis in a special cell to produce fairly pure HNO_3 (25-30% in concentration) and a mixture of KOH and KNO_3.

$$KNO_3 + H_2O = KOH + HNO_3$$

The power requirement is 0.5 to 0.7 kWh/gram mole KNO_3.

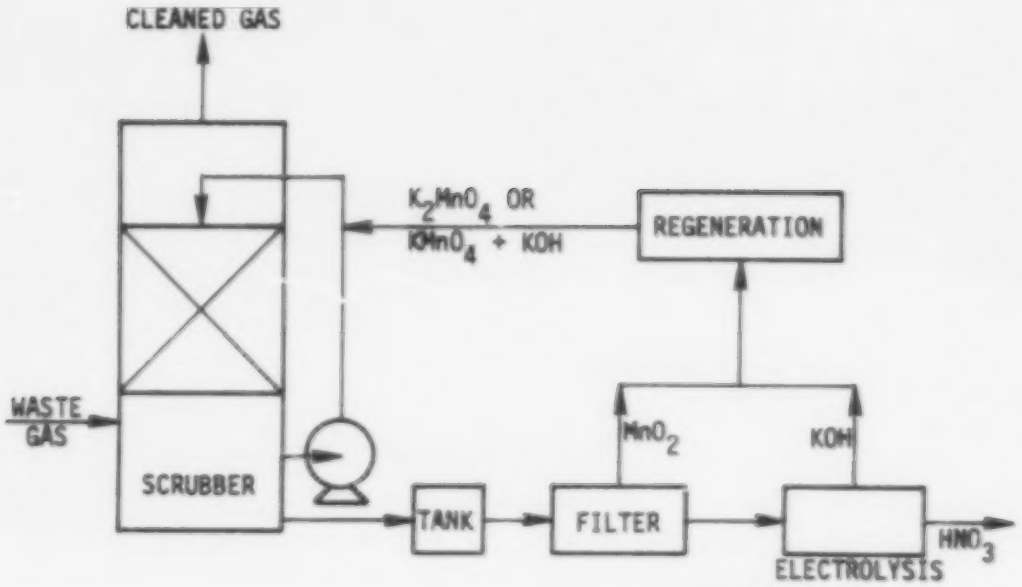


Figure 3-7. Flowsheet of Nissan permanganate process (NE-D process).

$$KMnO_4 + NO = KNO_3 + MnO_2$$
$$KNnO_4 + 2KOH + 3NO_2 = 3KNO_3 + MnO_2 + H_2O$$
$$2KMnO_4 + 4KOH + 3SO_2 = 3K_2SO_4 + 2MnO_2 + 2H_2O$$

Manganese dioxide is converted to alkali permanganate or manganate by a conventional process. The alkali nitrate (and sulfate) solution obtained is concentrated to produce a solid product, which can be used for fertilizer and other purposes. A simplified flowsheet is shown in Figure 3-8.

Evaluation

An advantage of the process is by-production of potassium nitrate, which is useful as fertilizer. The process must be costly, however, because it consumes potassium hydroxide and requires regeneration of potassium permanganate.

TESTS BY CRIEP ON SODIUM SULFITE SCRUBBING[8]

Background

CRIEP (The Central Research Institute for Electric Power Industry), which is financed by the nine major power companies of Japan, has performed extensive fundamental research in NO_x abatement including work on combustion control and wet and dry processes for NO_x removal from flue gas. CRIEP did laboratory work on NO absorption by a sodium sulfite solution containing a ferrous compound and performed tests with a small packed tower. CRIEP recently started to cooperate with Kureha Chemical in further development of the process.

Description of the Tests

Figure 3-9 shows the apparatus used in the laboratory tests. The adsorption column is 36 mm in diameter and 150 mm high. One liter of sodium sulfite solution (10%) was placed in the column to a depth of 100 mm. Nitrogen gas

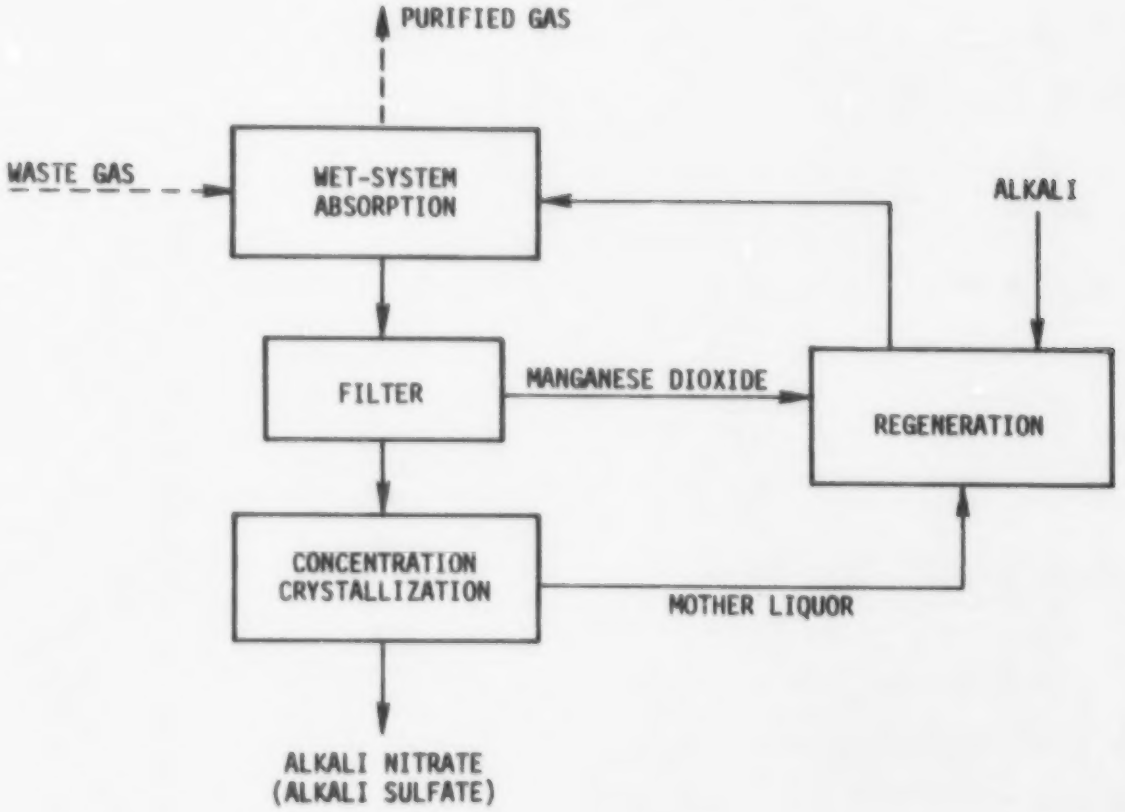
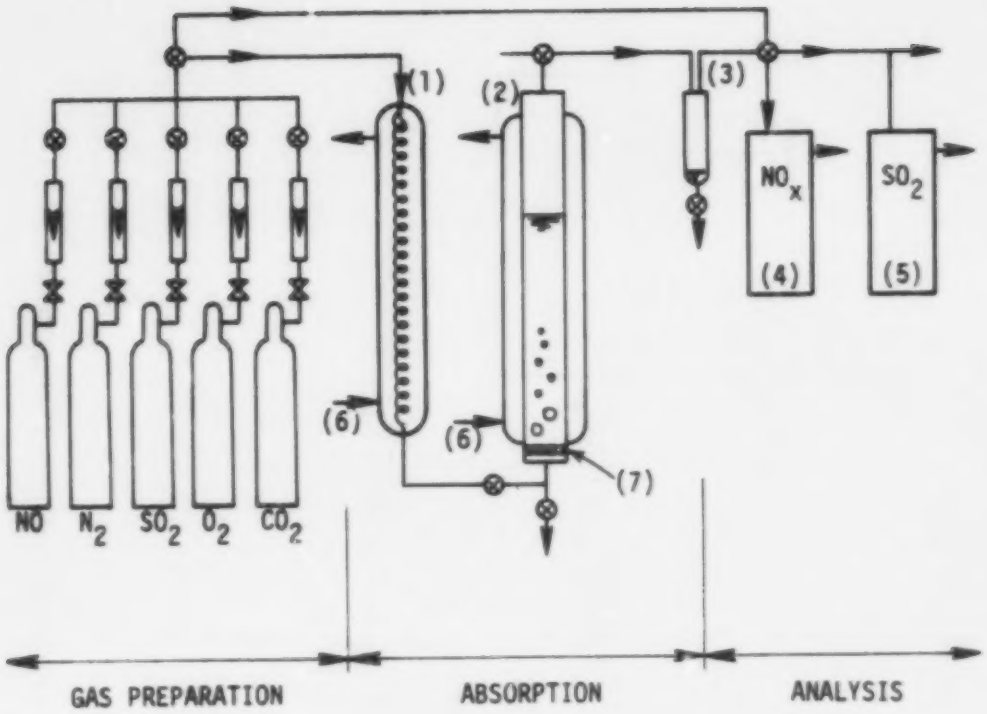


Figure 3-8. Simplified flowsheet of MON process.



(1) GAS HEATER (2) ABSORPTION COLUMN

(3) TRAP (4),(5) ANALYZER

(6) HOT WATER (7) POROUS PLATE

Figure 3-9. Apparatus for test (CRIEP).

containing 265 ppm NO was bubbled from the bottom of the column at a rate of 1.5 liters per minute into the solution kept at 50°C. Various additives were tested to promote the absorption. Ferrous sulfate and oxalate promoted the NO absorption remarkably, as shown in Table 3-2.

Table 3-2. EFFECT OF ADDITIVES ON NO_x REMOVAL

Form of additive	Concentration of additive, %	NO removal ratio, %	pH of liquor
None	None	15	9.8
$Fe(SO_4)_2$	0.3	95	6.6
CuCl	1	52	7.9
$Ni_2(SO_4)_3$	1	5	8.3
$CrCl_3$	1	18	7.5
$CoCl_3$	1	20	5.2
FeC_2O_4	1	98	7.8
$Cu(CH_3COO)_2$	0.1	34	7.3
SnC_2O_4	0.1	19	9.1

Ferrous hydroxide precipitates when the solution is neutral or alkaline. Addition of a small amount of ethylene diamine tetraacetic acid (EDTA) prevented the precipitation and further promoted the absorption. Figure 3-10 shows the relationship of NO removal ratio to the concentration of sodium sulfite solution containing a ferrous sulfate or ferrous chelate (EDTA) compound. The NO removal ratio reached more than 90 percent when the concentration of the sulfite was more than 5 percent with the ferrous sulfate and more than 0.4 percent with the ferrous chelate compound. High oxygen concentration in the gas considerably decreased the removal efficiency with the ferrous or ferric sulfate but only slightly with the ferrous or ferric chelate com-

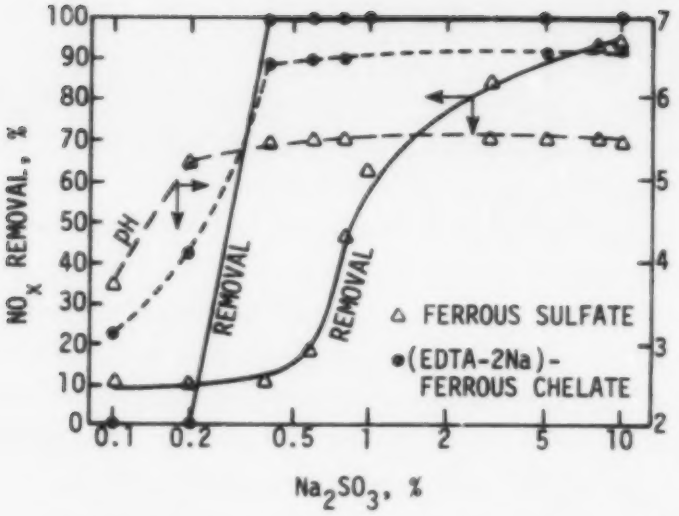
pound (Figure 3-11).

Further tests were carried out with a small tower 200 mm in diameter and 2 m in packing height packed with Tellerette. A gas containing 365 ppm NO, 930 ppm SO_2, and 3 percent O_2 was introduced from the bottom at a rate of 80 Nm^3/hr, while an absorbing liquor (10% sodium sulfite solution containing 0.02 mole/liter ferrous chelate compound at pH 6) was fed at a rate of 1800 liters/hr. The NO removal ratio was 43 percent, an indication that about a 10-m packing height was required for 90 percent removal. The SO_2 removal ratio was 98 percent. Tests are in progress to study the form of NO in the liquor and determine a way to reduce the absorbed NO into N_2.

Evaluation

NO is not easily absorbed in many kinds of liquors and is usually oxidized into NO_2 prior to scrubbing. In a sodium sulfite solution containing a ferrous compound, NO is absorbed fairly well. Although the absorption occurs slowly and requires a high tower, elimination of the oxidation step and expensive oxidizing agent is a considerable advantage of the process. It is desirable to develop a good way to convert the absorbed NO into a harmless or useful by-product.

Ferrous sulfate is not expensive but is affected by oxygen in flue gas. The ferrous chelate compound is not affected but is expensive and should not be lost during the treatments. Flue gas normally contains a small amount of chlorine, which tends to accumulate in the absorbing liquor and is usually purged with wastewater. The purge of water should be minimized or eliminated because it would cause the loss of the chelate compound.



ADDITIVE 0.01 mole/ℓ GAS 1.5 ℓ/min PLATE
ABSORBING LIQUOR 1.0 ℓ NO 275 ppm
ABSORBING LIQUOR 50°C

Figure 3-10. Effect of Na_2SO_3 concentration.

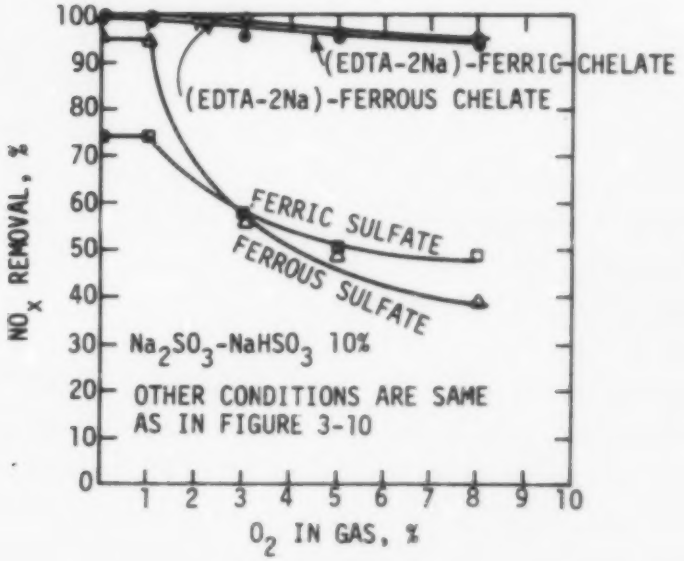


Figure 3-11. Effect of O_2 concentration.

Evaluation

The process may be suited for treating relatively small amounts of gas. Potassium hydroxide is costly, and the demand for potassium nitrate is limited. Therefore, the electrolysis of potassium nitrate to produce nitric acid and potassium hydroxide may be needed for treating large amounts of gas. The process, however, might be more costly than the acid, because the Nissan process involves two electrolysis decomposition. For flue gas containing SO_2, a desulfurization step should be applied first to reduce the consumption of potassium hydroxide and permanganate.

MON ALKALI PERMANGANATE PROCESS

Background

The process developers are Mitsubishi Metal Co., Mitsubishi Chemical Machinery Mfg. (MKK), and Nippon Chemical Industrial Co. Under the leadership of Professor T. Okabe, Tohoku University, these three companies have jointly developed the process. A pilot plant (300 Nm^3/hr flue gas from an oil-fired boiler) started operation in November 1972 removing both NO_x and SO_2. A large pilot plant (4000 Nm^3/hr) went into operation in December 1974 at the Omiya Research Station, Mitsubishi Metal, in which flue gas is first washed with a sodium hydroxide solution to remove SO_2 and is then subjected to NO_x removal.

Process Description

NO_x (and also SO_2) in waste gas are absorbed in an alkaline solution containing alkali permanganate or manganate--for example, a KOH solution containing $KNnO_4$. The NO_x (and SO_2) are absorbed and oxidized to form alkali nitrate and sulfate while permanganate or manganate is reduced to precipitate manganese dioxide, which is then filtered off.

KUREHA REDUCTION PROCESS

Background

The process developer is Kureha Chemical Industry Co. Kureha, a middle-size chemical company, has developed many new processes that have been used commercially, including those for oil gasification and wet desulfurization. Kureha has tested NO_x removal by a sodium sulfite solution containing a catalyst and acetic acid, which promote the reaction remarkably. A pilot plant with a capacity of treating 5000 Nm^3/hr of flue gas from an oil-fired boiler is under construction at the Nishiki Works of Kureha. The pilot test is assisted by the Federation of Electric Power Industry. The Central Research Institute for Electric Power Industry (CRIEP) recently started to cooperate with Kureha for fundamental research of the process.

Process Description

A schematic flowsheet of the process and major chemical reactions are shown in Figure 3-12. Flue gas containing SO_2 and NO_x is first introduced into a desulfurization unit (1) where SO_2 is absorbed by a sodium acetate solution to produce sodium sulfite and acetic acid. The treated gas is sent to an auxiliary NO_x removal unit (2) (some NO_2 is added to the gas and treated with a limestone slurry to remove NO_2 and equal amounts of NO). Calcium nitrite is by-produced. The remaining NO is then absorbed at a main NO_x removal unit (3) by a mixed solution of sodium sulfite and sulfate containing acetic acid and a catalyst. A compound $NH(SO_3Na)_2$ is formed by the absorption. The solution containing the compound and sodium sulfate is treated in a unit (5) with calcium acetate, to precipitate gypsum. The calcium acetate is obtained in a deacetation unit (4) by reaction of acetic acid and limestone. The liquor from the gypsum filter

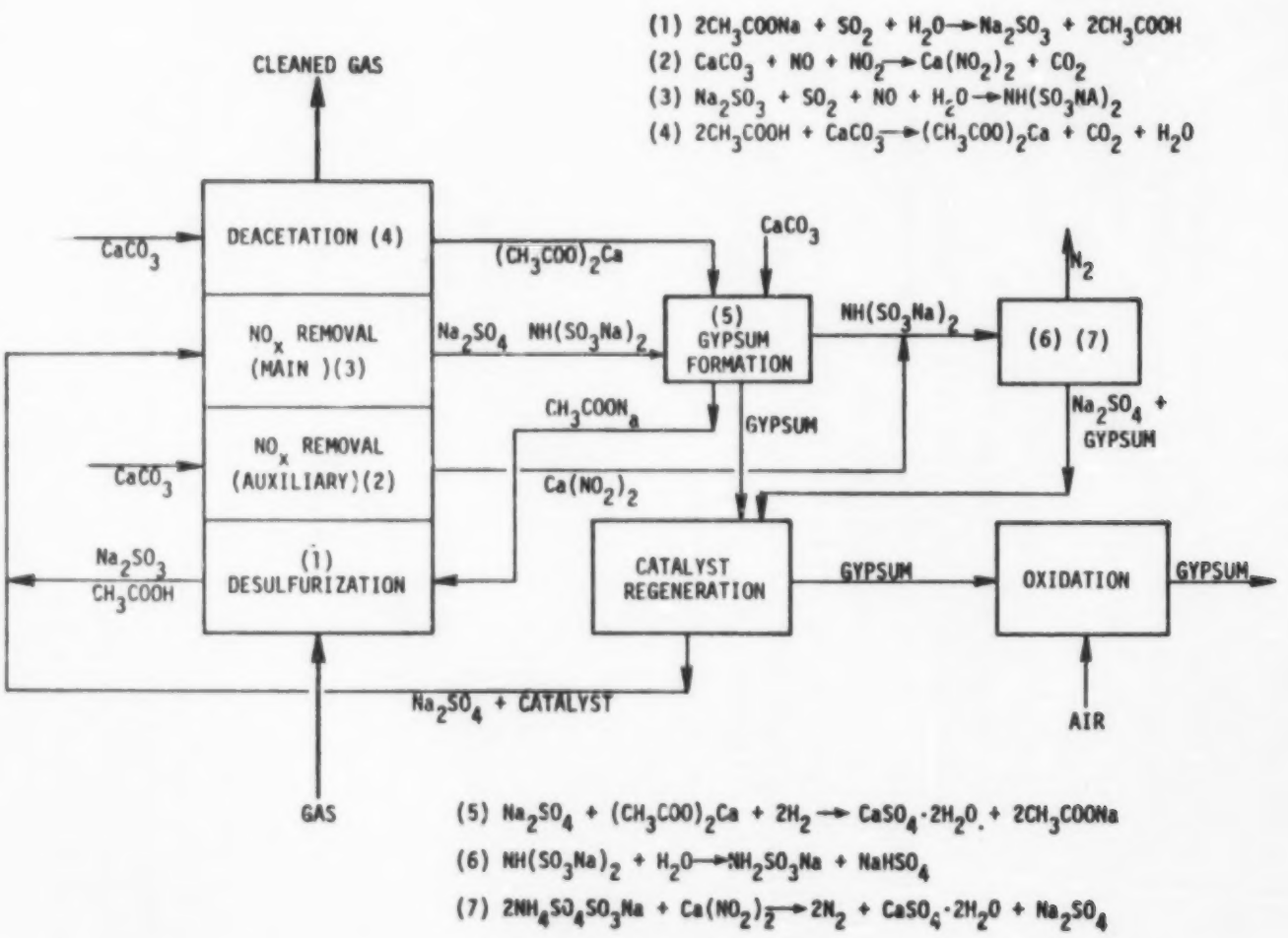


Figure 3-12. Flowsheet of Kureha process.

containing $NH(SO_3Na)_2$ is sent to a unit (6) in which the compound is hydralized to form NH_2SO_3Na, which is then reacted with calcium nitrite to release nitrogen gas and to by-produce gypsum and sodium sulfate (reactions 6 and 7). Gypsum is separated, and the liquor containing sodium sulfate and catalyst is sent through a catalyst regeneration unit to the main NO_x removal unit.

Evaluation

The process has the advantage of removing both SO_2 and NO_x while by-producing harmless nitrogen and useful gypsum. The process, however, is very complex and the plant seems costly and not easy to operate. Operational data of pilot plant are needed for further evaluation.

KAWASAKI MAGNESIUM PROCESS

Background

The process developer is Kawasaki Heavy Industries, one of the largest machine and plant manufacturers. They have developed SO_2 removal processes using both sodium scrubbing and magnesium scrubbing. Kawasaki also has tested a process for simultaneous removal of SO_2 and NO_x by magnesium scrubbing and is constructing a pilot plant with a capacity of treating 5000 Nm^3/hr of flue gas from a coal-fired boiler at the Taenake Power Station, Electric Power Development Co. The pilot plant is scheduled to go into operation in July 1975 under sponsorship of the Federation of Electric Power Industry.

Process Description

A flowsheet of the process is shown in Figure 3-13. The gas containing about 1000 ppm SO_2 and 400 ppm NO_x is mixed with NO_2 gas to adjust the NO_2/NO ratio to 1 and is treated with a magnesium hydroxide slurry to form magnesium sulfite

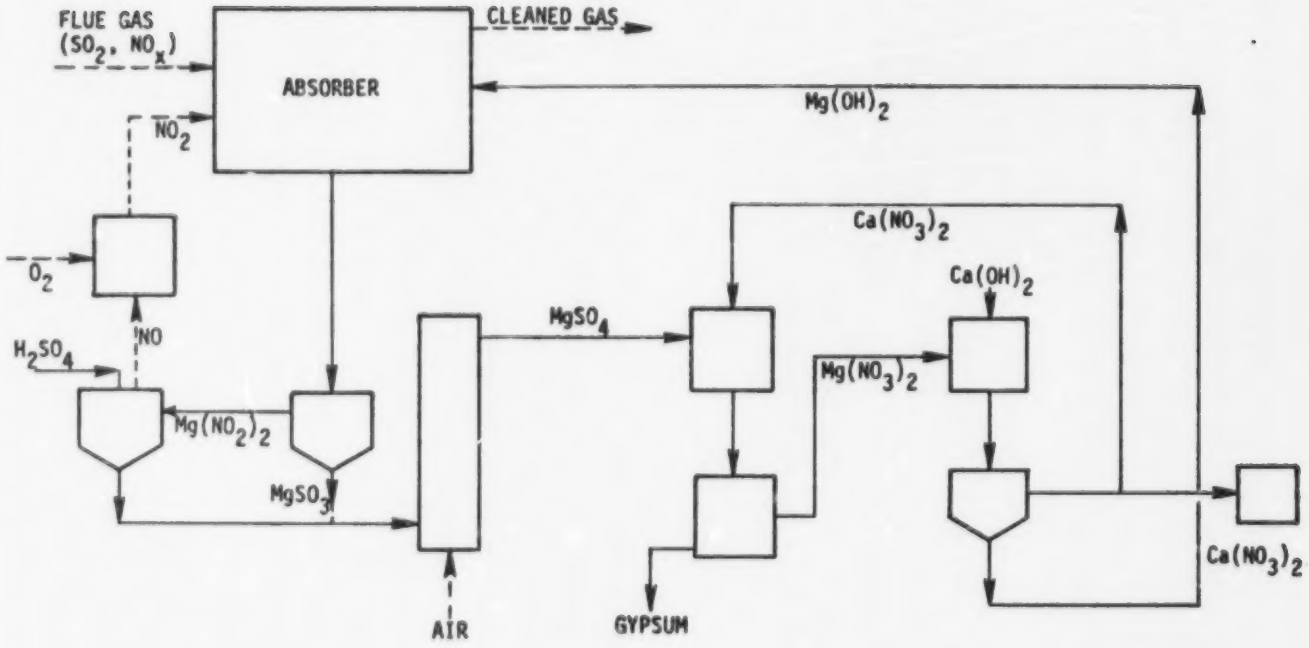


Figure 3-13. Flowsheet of Kawasaki magnesium process.

and nitrite. The nitrite is separated and decomposed by adding sulfuric acid to produce NO, which is oxidized to NO_2 and returned to the absorber. Magnesium sulfite is oxidized into sulfate and reacted with calcium nitrate to precipitate gypsum, which is returned to the absorber. The calcium nitrate liquor formed by the reaction is partly returned to the system for the reaction with magnesium sulfate and partly obtained as a by-product.

Advantages

The process removes both SO_2 and NO_x while by-producing salable gypsum and calcium nitrate, which may be used for fertilizer.

Disadvantages

The process is complex, and the plant may be costly. It may not be easy to attain high NO_x removal efficiency. The use of calcium nitrate is limited.

CHISSO AMMONIA SCRUBBING PROCESS

Background

The process developer is Chisso Corporation, a fertilizer producer that recently expanded to the petrochemical business. Chisso has developed a process for simultaneous removal of SO_2 and NO_x from flue gas by ammonia scrubbing using a catalyst to by-produce ammonium sulfate. A pilot plant (300 Nm^3/hr of flue gas from an oil-fired boiler) has been operated.

Process Description

A schematic flowsheet of the process is shown in Figure 3-14. Flue gas containing SO_2 and NO_x is absorbed with an ammoniacal solution containing a soluble catalyst to reduce the absorbed NO_x into NH_3 by ammonium sulfite and bisulfite, which are formed from SO_2 and ammonia. Most of the catalyst

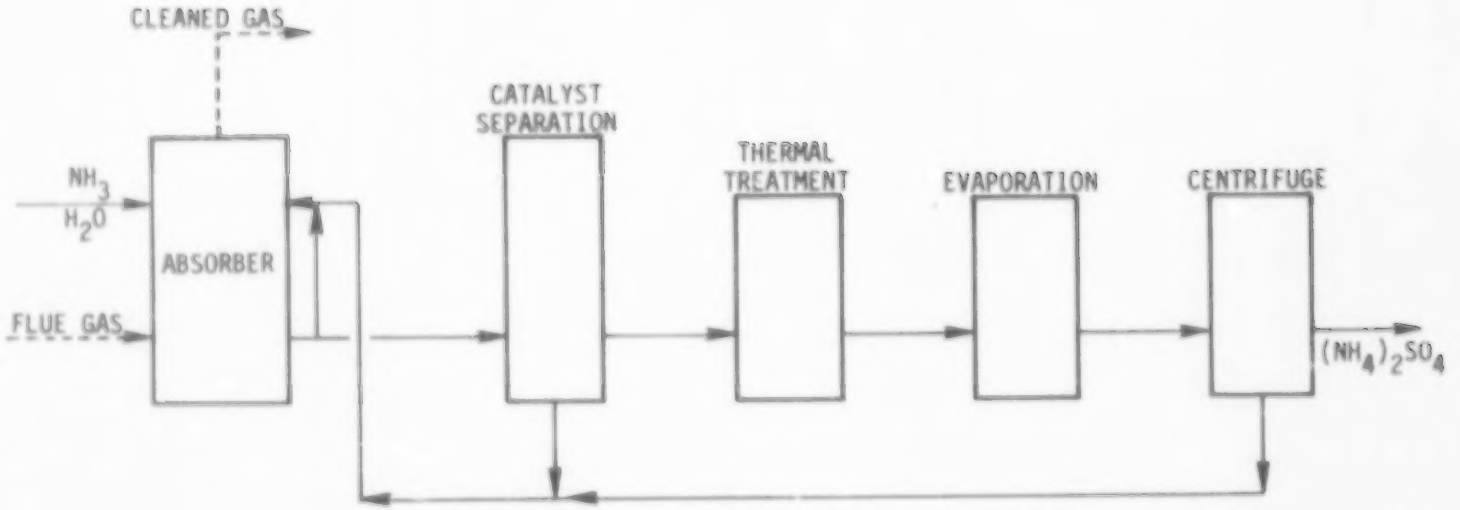


Figure 3-14. Simplified flowsheet of Chisso Process.

is separated from the product solution containing ammonium sulfate and sulfite and intermediate compounds. The solution is oxidized by air and then heated to convert the intermediate compounds into ammonium sulfate. The product solution is concentrated in an evaporator to crystallize ammonium sulfate, which is separated by a centrifuge. The mother liquor, which contains a small amount of the catalyst, is returned to the scrubber. The overall reaction may be expressed simply as follows:

$$2NO + 5SO_2 + 6NH_3 + 8H_2O = 5(NH_4)_2SO_4$$

For recovery of 80 percent of 200 ppm NO_x, the flue gas should have more than 1200 ppm SO_2.

Performance and Problems

The pilot plant has been operated for about a year. Reaction of NO_x with the sulfite liquor is slow. The removal ratios range from 60 to 80 percent. Use of a dilute liquor is favorable for the absorption but necessitates much evaporation for ammonium sulfate recovery. Therefore, NO_x removal of about 70 percent using a moderate concentration may be suitable. A portion of the catalyst is decomposed by the treatments. The catalyst is not affected by nickel and vanadium derived from flue gas. Chisso estimates the cost for simultaneous removal of SO_2 and NO_x to be about 30 percent more than the cost of SO_2 removal only.

Evaluation

The process has an advantage over other NO_x removal processes in that it gives a useful by-product from recovered SO_2 and NO_x. A disadvantage may be the difficulty in attaining a high NO_x removal ratio. Another difficulty is the possibility of plume formation, which is common to ammonia scrubbing processes. For further evaluation, operating data from a larger plant are required.

UBE ALKALI SCRUBBING PROCESS

Background

The process developer is Ube Industries Ltd. Ube, a large chemical company has operated a pilot plant for sodium scrubbing of tail gas from a nitric acid plant using a special type of scrubber. Commercial use of the process is under consideration.

Process Description

A flowsheet is shown in Figure 3-15. To attain an NO_2/NO mole ratio of about 1, the Ube process adds to the nitric acid plant tail gas, which contains 1000 to 3000 ppm NO_x and has a low ratio, a small portion of the process gas, which is rich in NO_2. The mixed gas is treated with an NaOH solution (about 3%) in a three- (or four-) stage tower with a liquid depth of about 500 mm at each stage. The relationship between the NO_2/NO mole ratio of the gas and NO_x concentration in the scrubber outlet gas is shown in Figure 3-16. Sodium nitrite and nitrate are recovered as by-products.

KOBE STEEL PROCESS

Kobe Steel Ltd. developed an SO_2 removal process using a calcium chloride solution. Kobe has measured NO_x removal for a pilot plant with a capacity of treating 1000 Nm^3/hr of flue gas from an oil-fired boiler or an iron ore sintering plant. NO_x is absorbed by a calcium chloride solution containing $Ca(OCl)_2$ as an oxidizing and neutralizing agent. By the reaction calcium nitrate is formed and chlorine is evolved, which is caught in a separate absorber by a calcium sulfite slurry to produce a calcium chloride solution and gypsum. It is said that a high NO_x removal ratio is attained. Corrosion may be a problem, however. Also, means

must be found for treating the by-products, calcium nitrate and chloride.

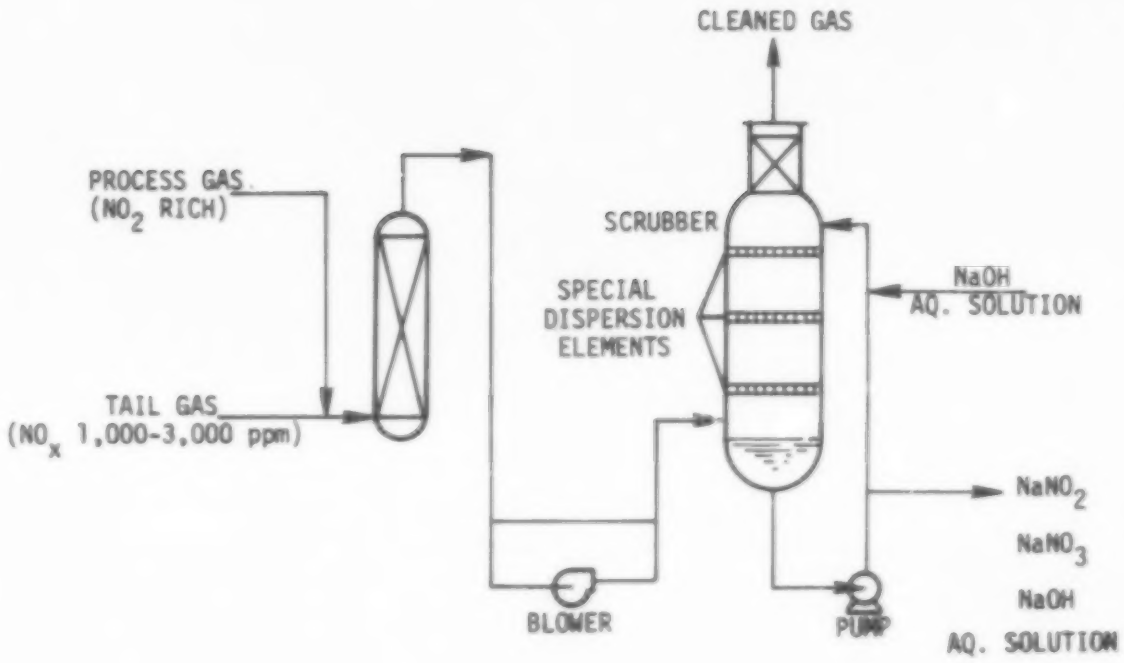


Figure 3-15. Flowsheet of Ube process.

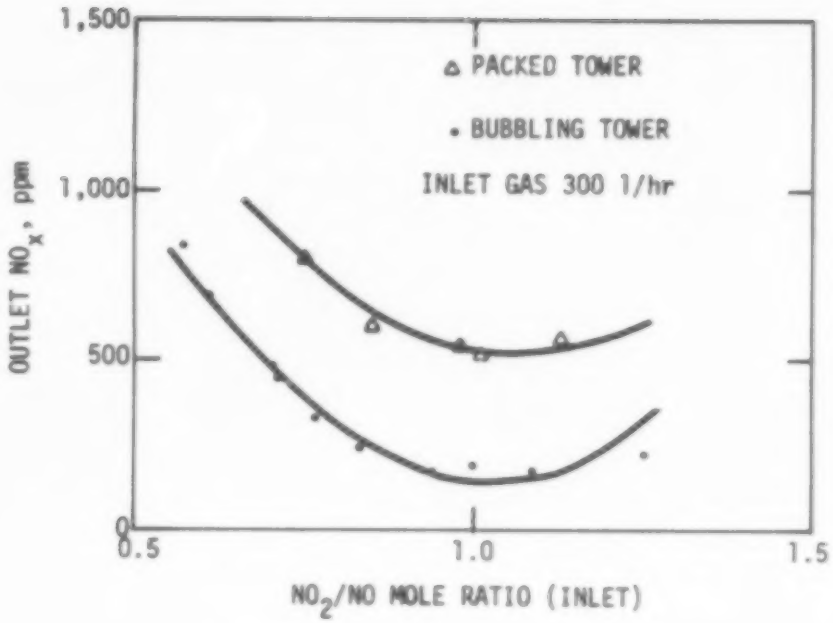


Figure 3-16. NO_2/NO ratio and NO_x removal.

4. DRY PROCESSES FOR DENITRIFICATION

GENERAL DESCRIPTION

Classification of Dry Processes

Dry processes for denitrification that have been developed in Japan may be classified as follows:

1. Catalytic reduction (selective, nonselective)
2. Catalytic decomposition
3. Electron beam radiation
4. Absorption (by molecular sieve, gelatinous silica, calcium silicate, etc.)

Among these, selective catalytic reduction has been used most widely. Electron beam radiation has been tested in a pilot plant. Small-scale tests of the dry absorption process have been made, but essentially no data are available.

Principle of Catalytic Reduction of NO_x

For treatment of tail gas at nitric acid plants, catalytic reduction of NO_x by H_2, CO, CH_4, etc., has been done for several years. As the catalyst, platinum carried on alumina is used because of its superior reactivity; more than 90 percent of the NO_x, which normally ranges in concentration from 500 to 3000 ppm in the tail gas, is reduced to N_2 at 500 to 800°C at a space velocity (SV) of over 30,000. For flue gas treatment, selective catalytic reduction by NH_3 is preferred because concentration of O_2 is much higher than that of NO_x and reducing gases such as H_2, CO, CH_4 are consumed mainly by O_2. Ammonia reacts not only with NO_x but also with O_2, as shown by the following reactions:

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad (1)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad (2)$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (3)$$
$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad (4)$$

The equilibrium constants of these reactions at various temperatures are shown in Figure 4-1.[10] The figure indicates that although the constant is the largest with reaction (1), other reactions can also proceed almost to completion at temperatures below 1000°C. Therefore, it is necessary to use a catalyst that promotes reaction (1) and delays the other reactions.

Platinum catalyst tends to promote reactions (3) and (4), which are undesirable, and moreover is readily poisoned by SO_2 and SO_3 in gas. Catalysts suitable for selective promotion of reaction (1) and more resistant to SO_x than platinum are being made from base metal oxides carried on alumina.

"Clean gas", such as that formed by burning of natural gas, is essentially free from SO_x and dust; this gas can undergo denitrification fairly easily by reaction with ammonia at 300 to 350°C with a base metal catalyst. The denitrification of "dirty gas", which contains considerable amounts of dust and SO_x, is not easy because those substances tend to contaminate the catalyst. Extensive studies have been made in Japan on the preparation of catalysts resistant to SO_x and dust. Although some of the catalysts are not poisoned by SO_2 when used at relatively high temperatures (350 to 450°C), most of them are affected by SO_3. Dust is a common retardant of catalytic action and should be minimized by the use of a highly efficient electrostatic precipitator or scrubber.

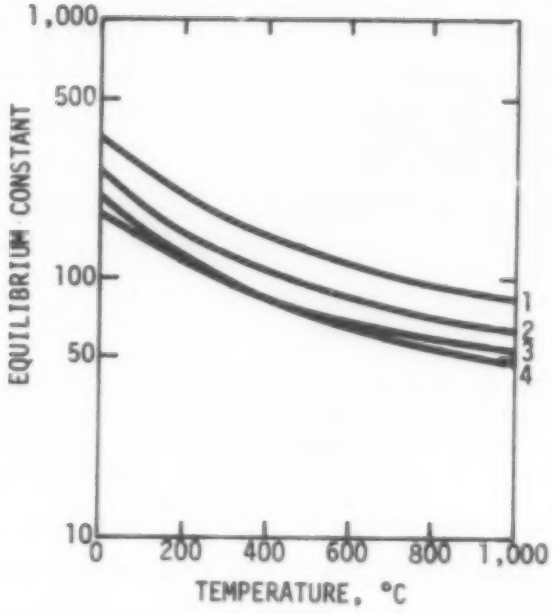


Figure 4-1. Equilibrium constants of reactions.

Pilot and Commercial Plants with Selective Catalytic Reduction (SCR) Processes

Many Japanese companies have developed their own catalysts and tested them in pilot plants. Commercial developers and pilot plants are shown in Table 4-1. Sumitomo Chemical, the most advanced in this field, has completed five commercial plants for processing of clean gas and is constructing two for dirty gas. Hitachi Shipbuilding is constructing two commercial plants for treatment of dirty gas; in this treatment, wet-process desulfurization will precede the denitrification.

Advantages and Disadvantages of the SCR Process

The SCR process has the following advantages:

1. Compared with nonselective catalytic reduction, SCR consumes much less reducing gas.

2. Compared with wet processes for NO_x removal, the SCR process is simple and requires less plant space. Moreover, SCR gives no troublesome by-products and necessitates no reheating of gas.

For removal of NO_x from clean flue gas, SCR may be the best of all denitrification processes so far developed. It has the following disadvantages, however, particularly in treatment of dirty gas.

1. Base-metal catalysts are not as reactive as noble-metal catalysts; SV's of 4,000 to 7,000 are normally used, as compared with a range of 50,000 to 150,000 with noble-metal catalysts. A large amount of catalyst and a large reactor are required.

2. Catalysts are affected by dust and most are poisoned by SO_3 and SO_2. Because the catalysts are made up of heavy metals, disposal of spent catalysts may pose some problem.

Table 4-1. MAJOR PLANTS FOR DENITRIFICATION BY SELECTIVE CATALYTIC REDUCTION

Process developer	Plant owner	Plant site	Capacity (Nm^3/hr)	Source of gas	Completion
Sumitomo Chemical	Sumitomo Chiba Chem.	Sodegaura	30,000	Oil-fired boiler	July 1973
Sumitomo Chemical	Higashi Nihon Methanol	Sodegaura	200,000[a]	Heating furnace	May 1974
Sumitomo Chemical	Nihon Ammonia	Sodegaura	250,000[a]	Heating furnace	Mar. 1975
Sumitomo Chemical	Sumitomo Chem.	Anegasaki	100,000[a]	Gas-fired boiler	Feb. 1975
Sumitomo Chemical	Sumitomo Chem.	Anegasaki	200,000[a]	Gas-fired boiler	Feb. 1975
Sumitomo Chemical	Sumitomo Chem.	Niihama	200,000[a]	Heating furnace	Mar. 1975
Sumitomo Chemical	Sumitomo Chem.	Sodegaura	250,000	Oil-fired boiler	May 1976
Sumitomo Chemical	Sumitomo Chem.	Sodegaura	300,000	Oil-fired boiler	May 1976
Hitachi Shipbuilding	Kansai Oil	Sakai	5,000	Oil-fired boiler	Nov. 1973
Hitachi Shipbuilding	Idemitsu Kosan	Chiba	350,000	CO-fired boiler	Nov. 1975
Hitachi Shipbuilding	Shindaikyowa Pet. Chem.	Yokkaichi	440,000	Oil-fired boiler	Nov. 1975
Tokyo Electric-Mitsubishi H.I.	Tokyo Electric	Minamiyokohama	10,000[a]	Gas-fired boiler	Jan. 1974
Kurabo	Kurabo	Hirakata	5,000	Oil-fired boiler	Nov. 1973
Kurabo	Kurabo	Hirakata	30,000	Oil-fired boiler	Aug. 1975
Kansai Electric-Hitachi Ltd.	Kansai Electric	Sakaiminato	4,000	Oil-fired boiler	Jan. 1975

Table 4-1 (continued). MAJOR PLANTS FOR DENITRIFICATION BY SELECTIVE CATALYTIC REDUCTION

Process developer	Plant owner	Plant site	Capacity (NM^3/hr)	Source of gas	Completion
Chubu-IHI-Mitsui Toatsu	Chubu Electric	Shinnagoya	8,000	Oil-fired boilers	Oct. 1974
Chubu-MKK	Chubu Electric	Yokkaichi	100	Oil-fired boilers	Oct. 1974
Mitsubishi H.I.	Mitsubishi H.I.	Hiroshima	4,000	Oil-fired boilers	Dec. 1974
Kobe Steel	Kobe Steel	Kakogawa	600	Sintering plant	May 1974

[a]Clean gas; those without superscript are for treatment of dirty gas.

3. For treatment of dirty gas, wet-process desulfurization may be carried out first to remove most of the dust, SO_3, and SO_2. In this case, the gas temperature drops to 50 to 60°C and must then be heated 350 to 400°C. A large heat exchanger and a considerable amount of fuel are needed. Mists from the scrubber may cause corrosion of the heat exchanger and contamination of the catalyst.

4. An NH_3/NO_x mole ratio of 1.0 to 1.5 is normally used, although the theoretical ratio is about 0.67. Although a portion of the excess ammonia decomposes in the reactor, a considerable amount of it would remain in the treated gas and may cause problems. For example, ammonia may combine with SO_3, which is present in a small amount even after the wet scrubbing, to form ammonium bisulfate. Tendency of the bisulfate to condense in a heat exchanger causes corrosion and decreases heat transmission.

5. A simple calculation indicates that treating half of the gas from stationary sources in Japan would require 600,000 tons of ammonia yearly, which is equivalent to two-thirds of the total nitrogen fertilizer consumption in Japan. Because it is estimated that the world's supply of nitrogen fertilizer will run short for at least several years, such a large amount of ammonia should be used for fertilizer.

SUMITOMO REDUCTION PROCESSES

Selective Catalytic Reduction

Sumitomo Chemical Industries Ltd., has conducted screening tests since 1971 with more than 1,000 catalysts with base-metal oxides carried on alumina for selective reduction of NO_x by ammonia. The tests have been both with dirty gas, containing SO_x and dust, and clean gas essentially free from those contaminants. A plant with a capacity to treat 30,000 Nm^3/hr of flue gas from an oil-fired boiler has been operated since July 1973. A commercial plant with a capacity of treating 200,000 Nm^3/hr of flue gas (clean gas

from LPG burning) from a reformer at the Sodegaura plant, Higashi Nihon Methanol Co. (HNM), went into operation in May 1974 (Figure 4-2). This may be the first commercial plant for flue gas denitrification in the world. Recently, operation of four more commercial plants for treatment of clean gas and construction of two commercial plants for treatment of dirty gas were started (Table 4-1).

Process Description

A flow sheet of the HNM plant is shown in Figure 4-3. Flue gas (clean gas) containing about 200 ppm NO_x (mainly NO) at 300 to 350°C is injected with ammonia at a NH_3/NO_x mole ratio of 1 and introduced into a reactor containing a base-metal catalyst. About 90 percent of the NO_x is reduced to N_2 by reaction with ammonia. The treated gas passes through a fan and heat exchanger to a stack.

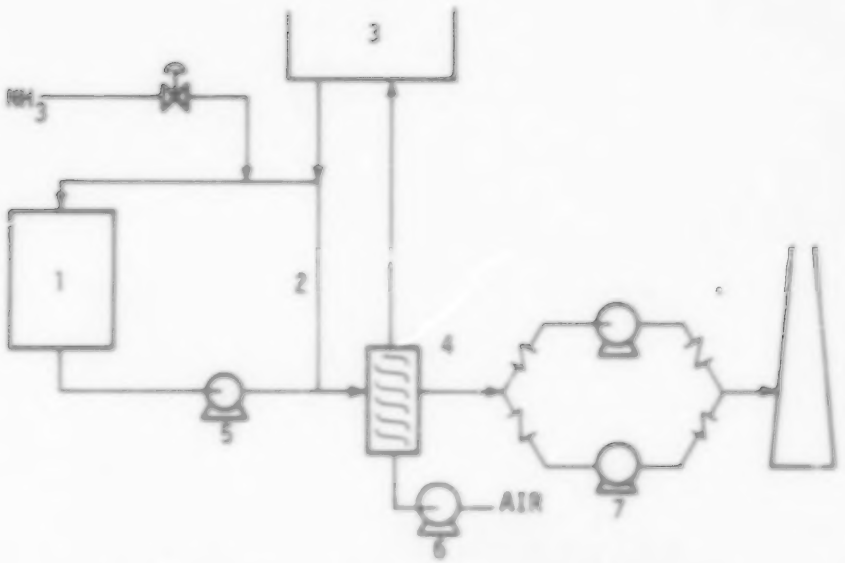
$$6NO + 4NH_3 = 5N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$

A schematic flow sheet of a plant for treatment of dirty gas is shown in Figure 4-4. The gas from an oil-fired boiler passes through an air heater, electrostatic precipitator, heat exchanger, and fan to a gas heater, where the temperature is adjusted to about 350°C. Ammonia is then added. The mixed gas is introduced into a reactor containing a SO_x-resistant catalyst and then passes through a heat exchanger and to a stack.

Status of Technology

Sumitomo has performed extensive basic studies with pilot plants. Figure 4-5 shows the relationship of NH_3/NO mole ratio to denitrification efficiency and ammonia content of the treated gas when a catalyst C-1 was used for clean gas at 300°C and 350°C with a space velocity (SV) of 7000.

Figure 4-2. NO_x removal plant (HNM).



1: REACTOR 2: BY-PASS 3: REFORMER
4: HEAT EXCHANGER 5,6,7 FAN

Figure 4-3. Flowsheet of denitrification process.[9]
(HNM, clean gas)

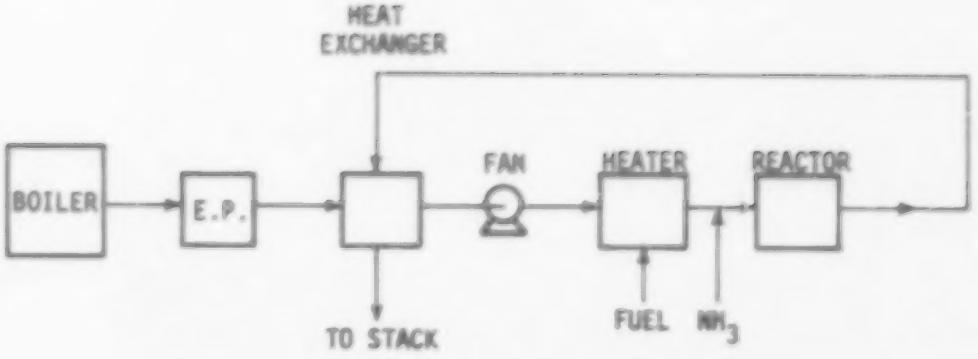


Figure 4-4. Flowsheet for dirty gas treatment.

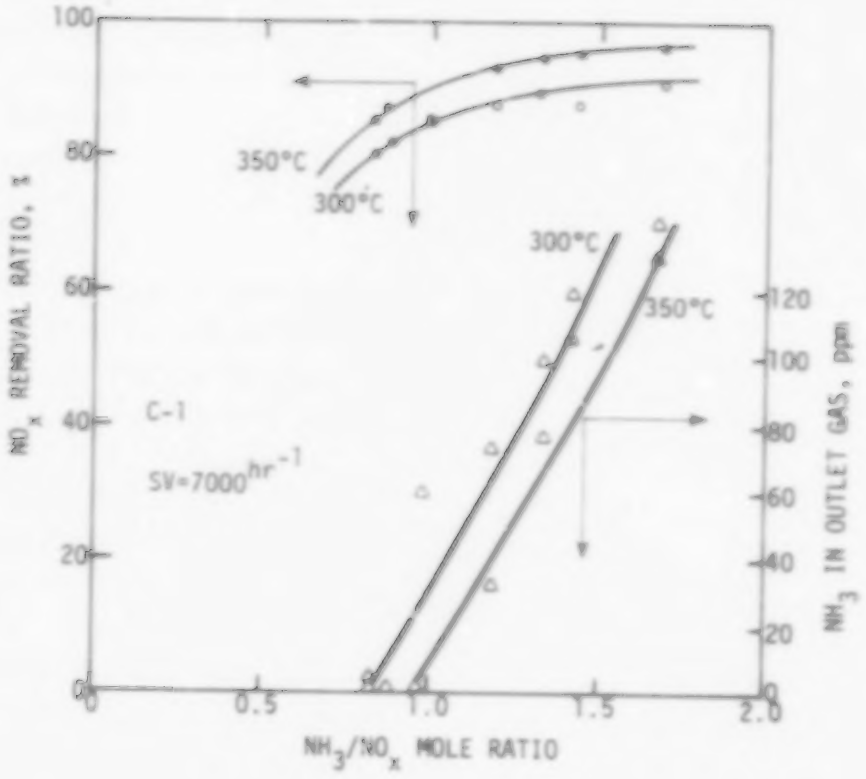


Figure 4-5. Effect of NH_3/NO_x mole ratio on NO removal and ammonia emission.

When the mole ratio was larger than 1, the efficiency exceeded 90 percent at 350°C and 85 percent at 300°C but the treated gas contained a considerable amount of ammonia. The ammonia concentration in the gas was higher at 300°C than at 350°C.

Figure 4-6 shows the effect of using catalyst A for the decomposition of excessive ammonia together with catalyst C-1. The ammonia concentration in the treated gas was kept below 5 ppm even at the mole ratio 1.5 by the effect of the catalyst A, while the denitrification efficiency stayed the same or slightly increased.

Sumitomo has also developed catalysts resistant to SO_x. Figure 4-7 shows the denitrification efficiencies of catalysts D and C-1 before and after being exposed to SO_3-containing gas. Catalyst D was not affected appreciably by SO_3, while C-1 was seriously affected.

Other tests with catalyst D showed that the denitrification efficiency was slightly higher with a gas containing 600 ppm NO_x than with a gas containing 100 ppm NO_x. Oxygen content of the gas above 1 percent showed no effect on efficiency, which was a little lower with a gas containing no oxygen. Water vapor showed no appreciable effect, although there was a slight tendency toward lower efficiency at high concentrations of water vapor.

Tests were also made on the formation of ammonium bisulfate deposits in the heat exchanger. The relationship of formation temperature to SO_3 and NH_3 concentrations is shown in Figure 4-8. Deposits may be prevented by keeping the temperature higher or concentrations lower than the values indicated in the figure.

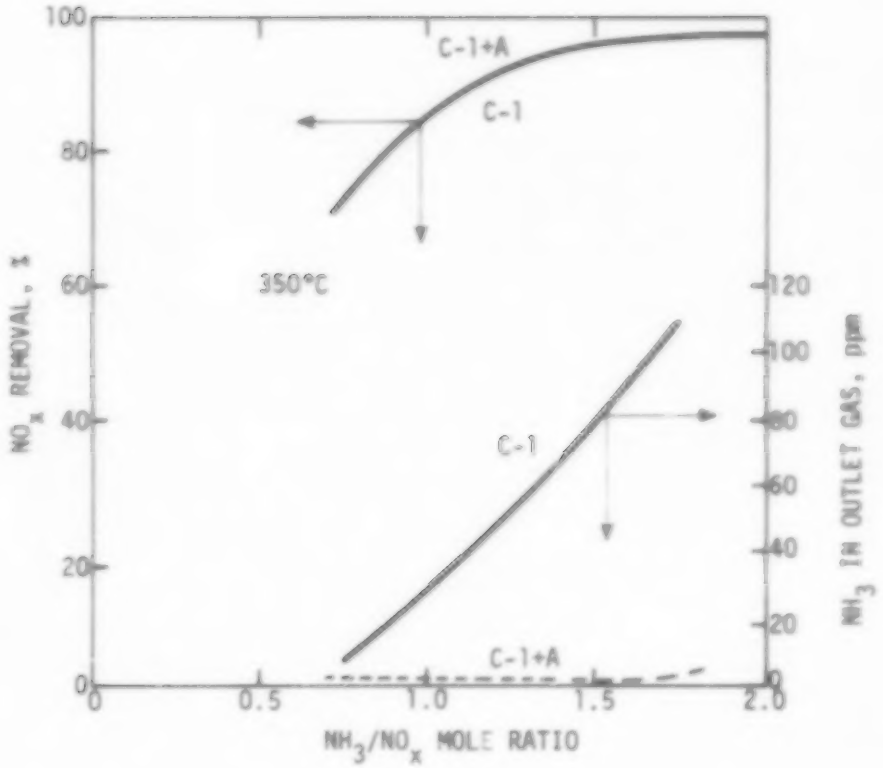


Figure 4-6. Effect of ammonia decomposition composition (A).

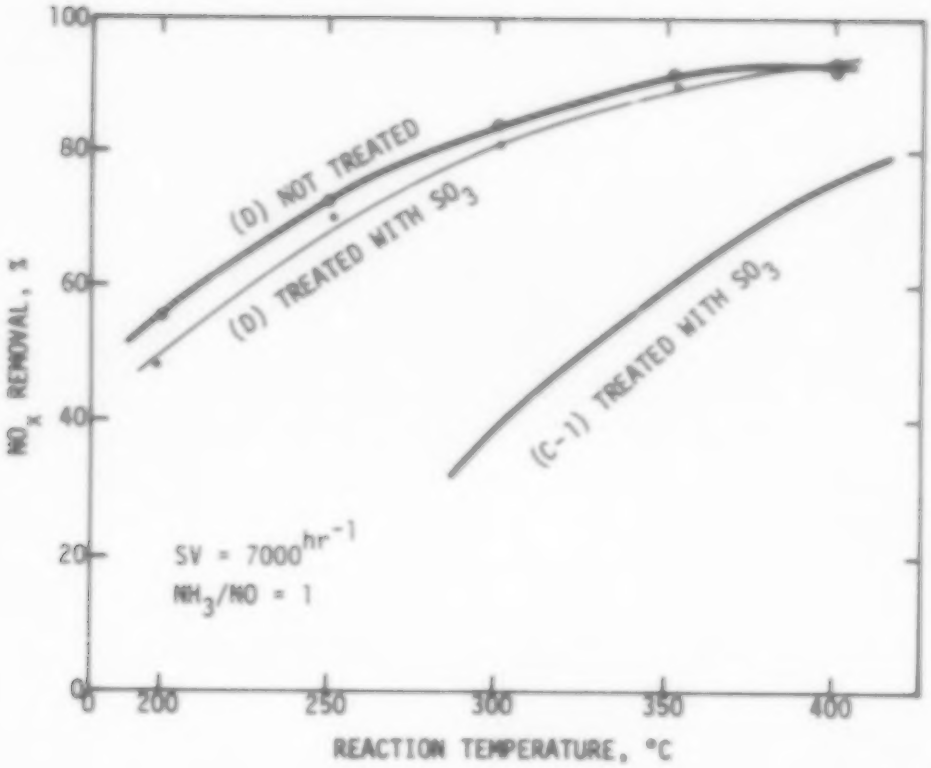


Figure 4-7. Effect of SO_3 on catalyst activity.

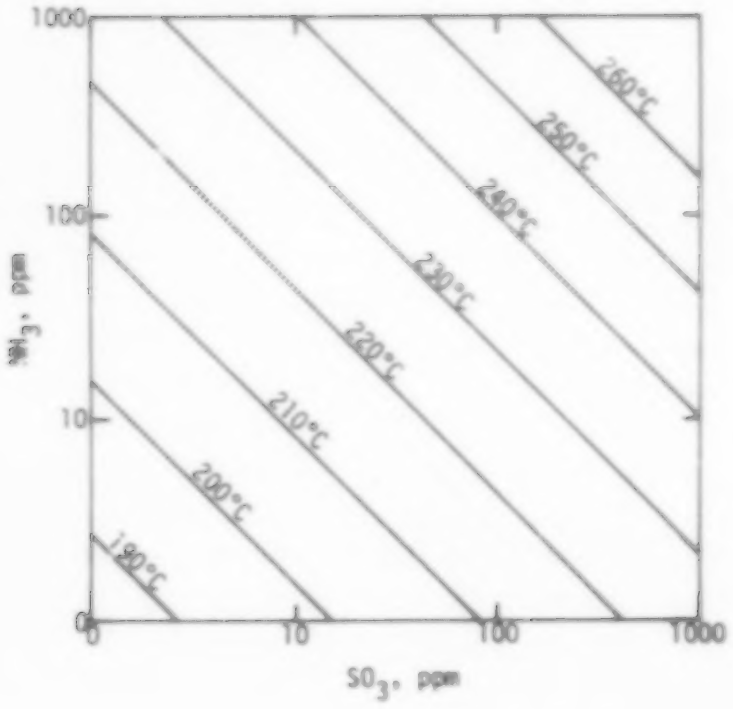


Figure 4-8. Formation temperature of NH_4HSO_4.

$$(NH_3\ (Gas) + SO_3\ (Gas) + H_2O\ (Gas) \rightleftarrows NH_4HSO_4\ (Liquid))$$

Performance of the Plants

The HNM plant was operated for 5 months continuously without trouble after its start-up in May 1974. Operation of the methanol plant and of the denitrification plant was then discontinued for a few months because of over-production of methanol but was resumed in February 1975. The flue gas, derived from the burning of LPG and an off-gas, normally contains about 200 ppm NO_x and 7 percent O_2. More than 90 percent of the NO_x is removed at a temperature of 300°C, an NH_3/NO_x mole ratio of 1, and an SV of 5000 to 7000. The activity of the catalyst has shown essentially no change since start-up. Some of the operation data, shown in Figure 4-9, agree well with those of the basic tests, indicating that the problems involving scale-up were solved by adequate engineering. The denitrification efficiency was kept above 90 percent even when the gas volume fluctuated and reached 250,000 Nm^3/hr. Concentration of ammonia in the treated gas was kept below 1 ppm by the use of the decomposition catalyst.

The pilot plant for treatment of the oil-fired (dirty) flue gas has been operated for over 4000 hours with no serious problem. The gas normally contains 200 ppm NO_x (mainly NO) 730 ppm SO_2, 30 to 40 ppm SO_3, 5 percent O_2 to 10 percent H_2O, 12.4 percent CO_2, and 72.6 percent N_2. Dust content is kept at 10 to 15 ppm by an electrostatic precipitator. More than 85 percent of the NO_x has been removed at temperatures of 330 to 350°C, an NH_3/NO_x mole ratio of 1 to 1.5, and an SV of 4000 to 6000. Result of a catalyst life test is shown in Figure 4-10. Dust concentrations will be kept below 10 ppm in commercial plants now under construction for dirty gas treatment.

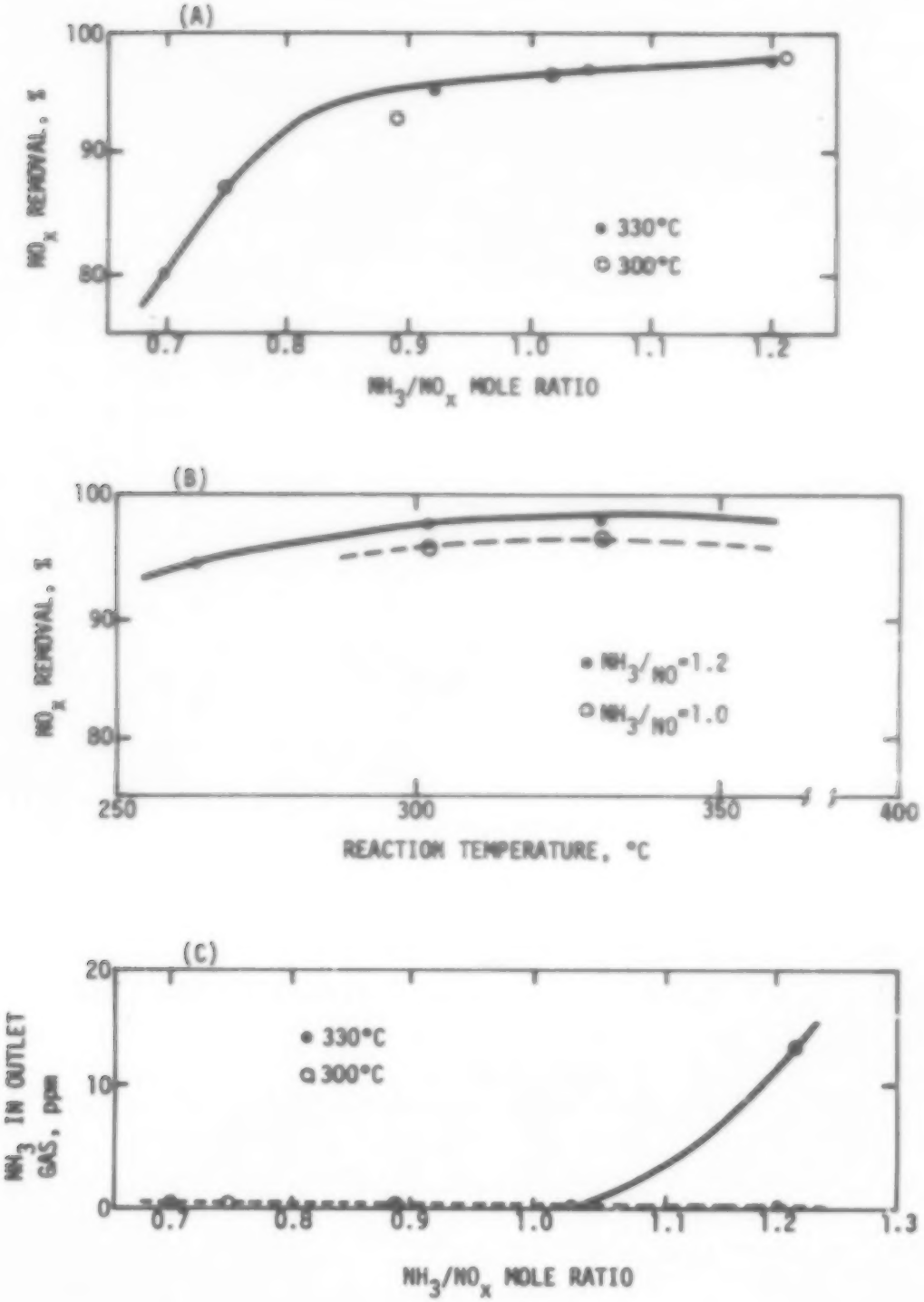


Figure 4-9. Operation data of HNM plant.

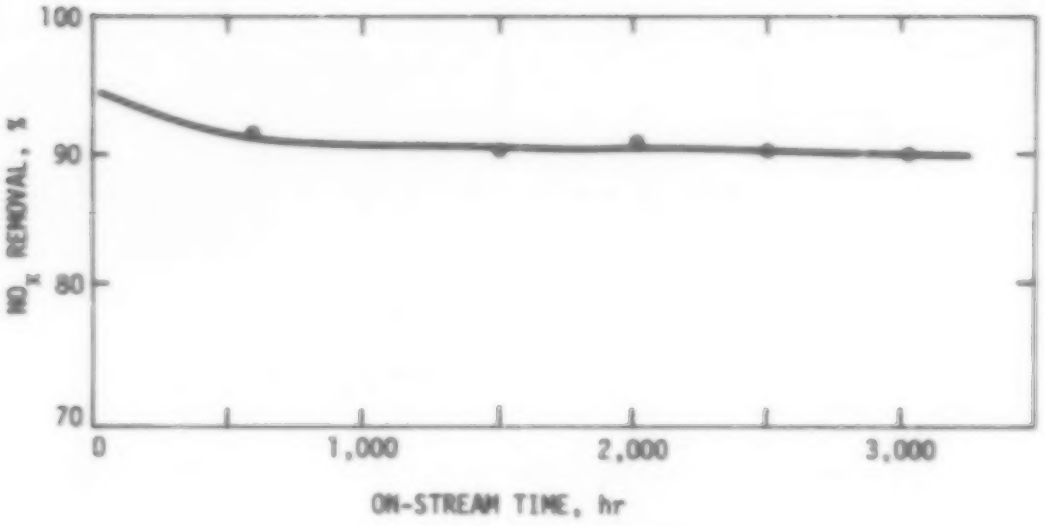


Figure 4-10. Result of life test (catalyst D, dirty gas) (NH_3/NO_x = 1.0 - 1.8, SV = 4,000, 330°C).

Economics

Estimates of the plant cost and denitrification cost (including depreciation for 7 years) are as follows:

Time of estimation	Spring 1973
Plant	HNM
Capacity, 1000 Nm^3/hr	200
Plant cost, $1000	830
Denitrification cost, ¢/1000 Nm^3	40
Plant cost, $/kW	12.6
Denitrification cost, (mil/kWh)	1.2

The HNM plant requires about 30 kg/hr of ammonia and about 800 kW power for a blower to compensate for the pressure drop of the gas through the reactor.

The plant of Nihon Ammonia (250,000 Nm^3/hr, clean gas) cost $2 million ($25/kW). The present cost for a new plant may be about $35/kW for clean gas. The cost may be more than $80/kW for treatment of dirty gas, including a highly efficient electrostatic precipitator but excluding a desulfurization unit.

Evaluation

The process is simple and plant operation is smooth. Resistivity of the catalyst to SO_x and very low emissions of NH_3 are other advantages. The process may be one of the best now available for flue gas denitrification. On the other hand, the plant cost and cost for denitrification of dirty gas are quite high, although they may not be higher than costs of other processes. Operation of the commercial plants for dirty gas treatment will provide a basis for further evaluation.

Nonselective Catalytic Reduction

Sumitomo developed a process to treat tail gas from a nitric acid plant containing 500 to 2000 ppm NO_x with 2 to 3 percent O_2. The NO_x is reduced to N_2 by reaction with hydrocarbons such as methane in the presence of a platinum catalyst carried on alumina.

$$4NO + CH_4 = CO_2 + 2H_2O + 2N_2$$
$$2NO_2 + CH_4 = CO_2 + 2H_2O + N_2$$

A commercial plant with a capacity of treating 22,500 Nm^3/hr of tail gas was completed in August 1968. Another plant (60,000 Nm^3/hr) went into operation in November 1972.

Process Description

A flowsheet of the process is shown in Figure 4-11. The tail gas containing 500 to 1000 ppm NO_x with 2.2 to 2.4 percent O_2 is heated to 430°C, mixed with methane (at 1.2 stoichiometry), and introduced into a reactor with a commercial honeycomb-type platinum catalyst at 6.5 kg/cm^2 pressure. More than 90 percent of the NO_x is reduced to N_2 at SV 50,000 to 120,000. A considerable portion of the methane is burned by O_2 in the gas, and the temperature reaches 730°C. The gas leaving the reactor at 730°C and containing 50 to 70 ppm NO_x passes through a waste-heat boiler and expander, where heat and energy are recovered, and then goes to a stack.

Economics

In 1968 the plant cost for 22,500 Nm^3/hr tail gas treatment was $150,000. The denitrification cost, including depreciation, was 20¢/1000 Nm^3.

Evaluation

This process is suitable for gases containing 300 to 5000 ppm NO_x with less than 3 percent O_2 and no SO_x or dust, and also for plants that can utilize the recovered energy

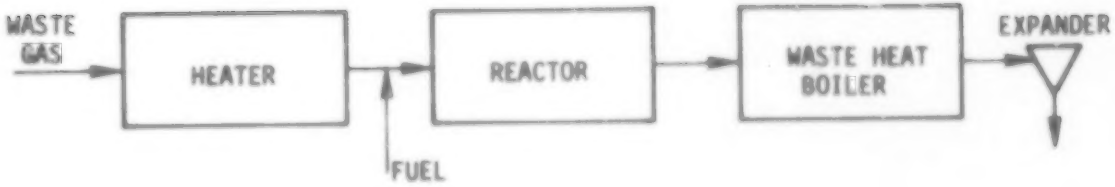


Figure 4-11. Simplified flowsheet of non-selective catalytic reduction process.

and heat. Too much O_2 in the gas would raise the reaction temperature exceedingly and could harm the catalyst. The platinum catalyst is effective but is poisoned by SO_x. A small amount of methane is discharged with the treated gas.

HITACHI SHIPBUILDING SCR PROCESS

Background

The process developer is Hitachi Shipbuilding and Engineering Co. Hitachi developed a base-metal catalyst for reduction of NO_x with ammonia and operated a pilot plant with a capacity of treating 5000 Nm^3/hr of flue gas from an oil-fired boiler from November 1972 to May 1974. Hitachi operates another pilot plant with a capacity of treating 2000 Nm^3/hr of flue gas from burning of LNG. Life tests of the catalysts have been carried out since June 1974 in a small test unit with oil-fired flue gas. Tests will be made with waste gas from an iron-ore sintering plant, a coke oven, a cement kiln, and similar operations.

Hitachi Shipbuilding is now constructing two commercial units. One is for Idemitsu Kosan (Chiba plant, 350,000 Nm^3/hr of refinery flue gas containing some SO_2). The other is for Shindaikyowa Petrochemical Co. (Yokkaichi plant, 440,000 Nm^3/hr of flue gas from an oil-fired industrial boiler). Both are to be completed by fall 1975.

Process Description

Flue gas is heated to 300 to 350°C by a heat exchanger and then to 400 to 450°C by a heater (Figure 4-12). Ammonia is injected, (NH_3/NO_x mole ratio of about 1), and the gas is then introduced into a reactor containing a base-metal catalyst. About 90 percent of the NO_x is reduced to N_2. The gas discharged from the reactor passes through the heat exchanger and then goes to a stack.

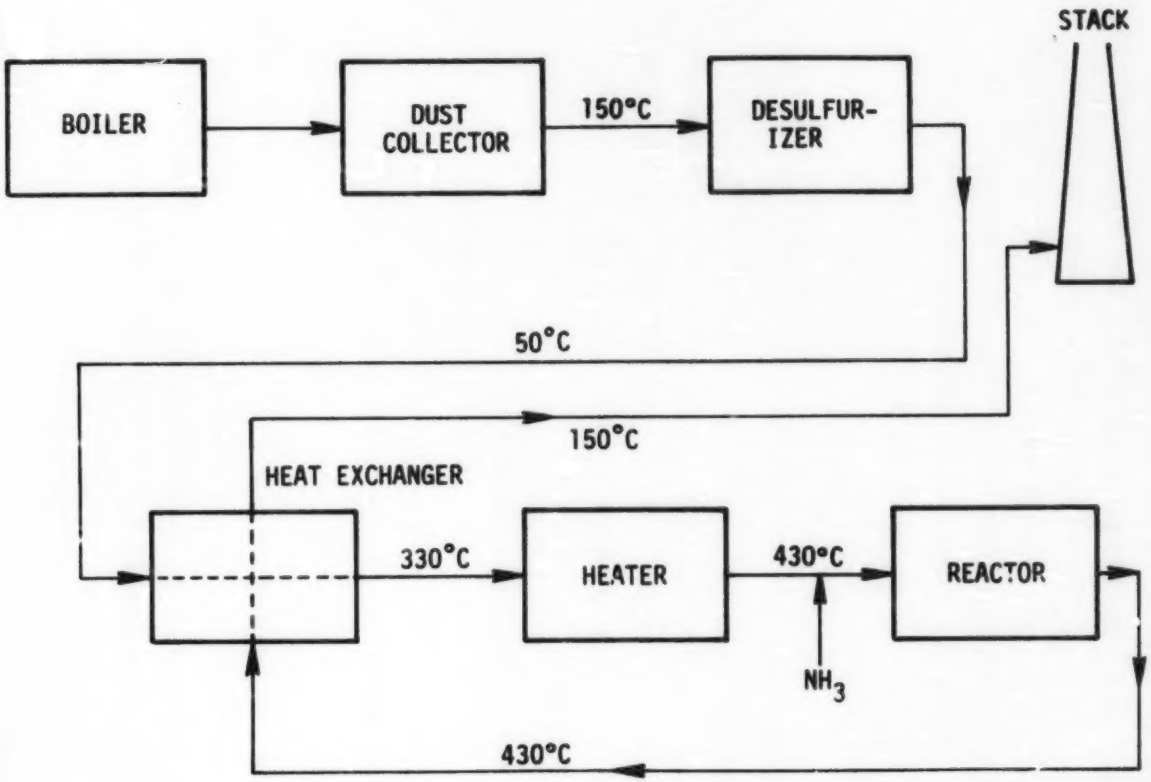


Figure 4-12. Flowsheet of Hitachi Shipbuilding process (An example of dirty gas treatment).

At the Yokkaichi plant, Shindaikyowa Petrochemical Co., the flue gas from an oil-fired boiler containing a considerable amount of SO_2 will be first treated by the Wellman-Lord process for removal of SO_x and dust. This plant would be the first commercial plant in the world for denitrification of dirty flue gas in combination with desulfurization. At the Chiba plant, Idemitsu Kosan, the flue gas from a refinery containing some SO_2 and dust will be introduced into the reactor without desulfurization.

Economics

The investment cost for a 100-MW unit is estimated to be $6 million, which is about equal to a desulfurization unit with an equal capacity operating by the wet process. The requirement of the treatment of 300,000 Nm^3/hr of flue gas, assuming 90 percent removal of 200 ppm NO_x, is estimated to be as follows:

Electric power	1850 kW
Fuel	10.6 million kcal/hr
Ammonia	36.5 kg/hr
Cooling water	30 t/hr (can be recycled)

Evaluation

The catalyst is resistant to SO_2. The process also has the advantages and disadvantages common to selective catalytic reduction processes as described earlier. Further evaluation will follow operation of the two commercial plants.

KURABO SCR PROCESS

Background

The process developer is Kurabo Industries. Kurabo, originally a textile company, recently went into the pollu-

tion control business and has constructed about one hundred relatively small commercial plants for removal of SO_2 by sodium scrubbing. Kurabo has also developed an SCR process for removal of NO_x and operated a pilot plant with a capacity of treating 5000 Nm^3/hr of flue gas from an oil-fired boiler. A plant (30,000 Nm^3/hr of flue gas from an oil-fired boiler) will be completed by November 1975.

Process Description

Flue gas containing dust and SO_x is mixed with ammonia at an NH_3/NO_x mole ratio of 1.2 and introduced at 420°C into a reactor, which has a moving bed of a catalyst made of copper and alumina, for example. More than 90 percent of the NO_x is converted into N_2. The catalyst, contaminated by the dust and SO_x, is sent to a regeneration step. After dust removal treatment, the catalyst is electrically heated to remove sulfur and carbon and to recover its activity. The regenerated catalyst is returned to the reactor. The gas discharged from the calciner is added to the outlet gas from the reactor and sent to a desulfurization unit. The process flow is shown in Figure 4-13.

Performance

Tests on the pilot plant with flue gas containing about 300 ppm NO_x and 500 to 2000 ppm SO_2 gave the following results:

NO_x removal	More than 90%
Dust removal	More than 80%
Operation temperature	420°C
Space velocity	7000
Pressure drop in the reactor	100 mm H_2O

The time for one cycle of the catalyst including regeneration was 100 to 200 hours.

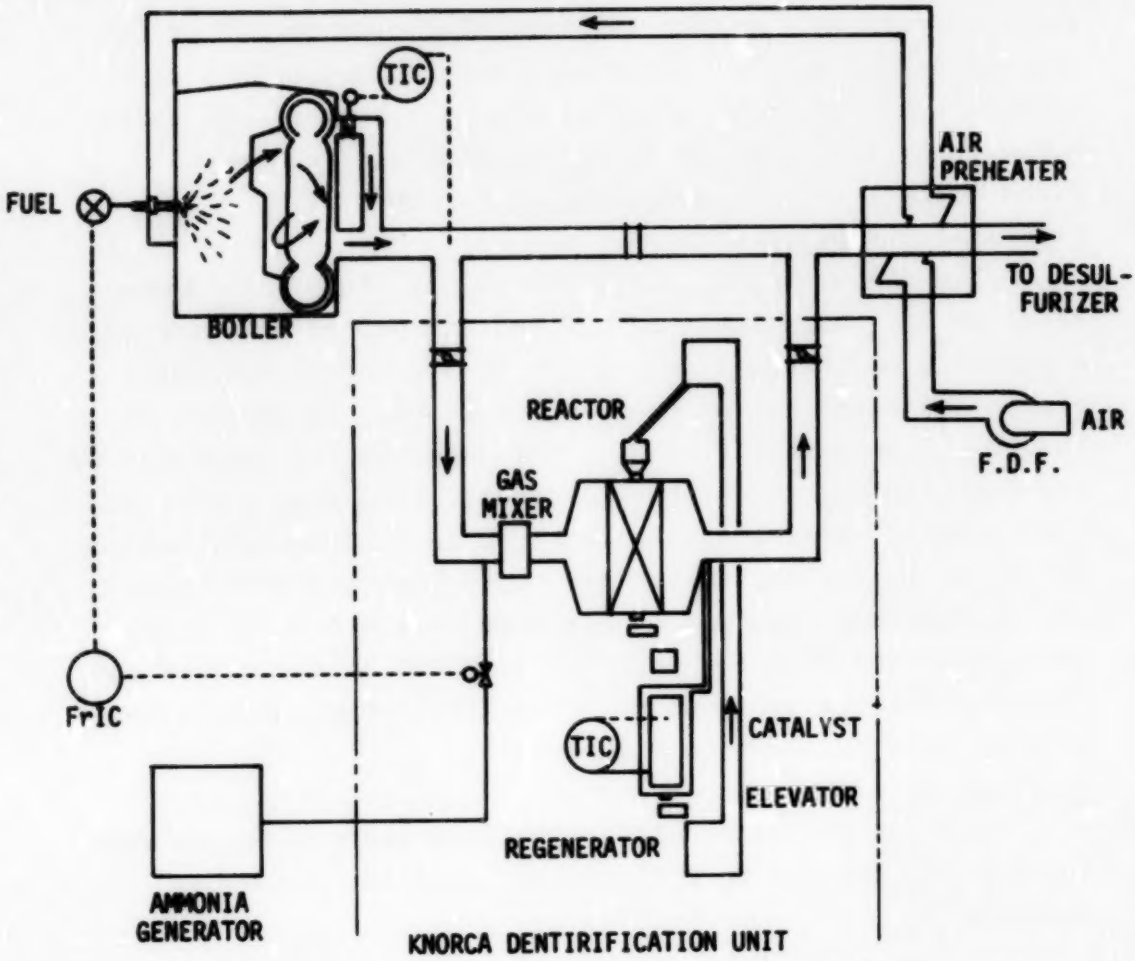


Figure 4-13. Flowsheet of Kurabo SCR process.

Evaluation

In this process, flue gas is subjected first to denitrification and then to desulfurization; in most other SCR processes the gas is first subjected to wet-process desulfurization and then to denitrification, which requires much energy for reheating. Thus, energy saving is an advantage of the process.

On the negative side, the electrical heating would add considerably to the cost and might cause some degradation of the catalyst. For the desulfurization, ammonia scrubbing such as developed by Kurabo may be suitable, but use of other processes may present some problem because of the presence of ammonia in the gas discharged from the NO_x removal step. Operation of the semicommercial plant will yield data for further evaluation.

TESTS ON SCR CATALYSTS BY CRIEP[10]

The Central Research Institute of Electric Power Industry (CRIEP) tested the reactivity of catalysts in a laboratory. Both commercial and synthetic catalysts (6 milliliters in a fixed bed) were tested at 100 to 500°C with 60 normal liters per hour of gas (SV 10,000) containing 220 to 260 ppm NO, 300 to 350 ppm NH_3, 3 to 4 percent O_2, and 1100 ppm SO_2. Some of the results with commercial catalysts with an alumina carrier (G-41, V-0701, and G-51) and synthetic catalysts with a granular reactive alumina carrier (2 to 4 mm, calcined at 550°C) are shown in Figure 4-14. The results show that copper and chromium catalysts give high reactivity at 300 to 350°C even in the presence of SO_2.

Figure 4-15 shows results of tests with copper catalysts on different carriers as specified in Table 4-2. The best results were obtained with bauxite (from Australia),

Table 4-2. COMPOSITION AND PROPERTY OF CARRIERS

Carrier	Composition of raw material, %						Specific surface area of calcined carrier, m^2/g
	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	Loss on ignition, %	
Active alumina	82.2	10.1	1.7	3.3	-	2.7	367
Bauxite	58.0	3.8	7.3	-	2.3	28.5	210
Kanuma earth	35.6	48.2	2.6	-	-	13.5	227
Active silica earth	12.5	76.1	1.5	0.4	-	8.0	272

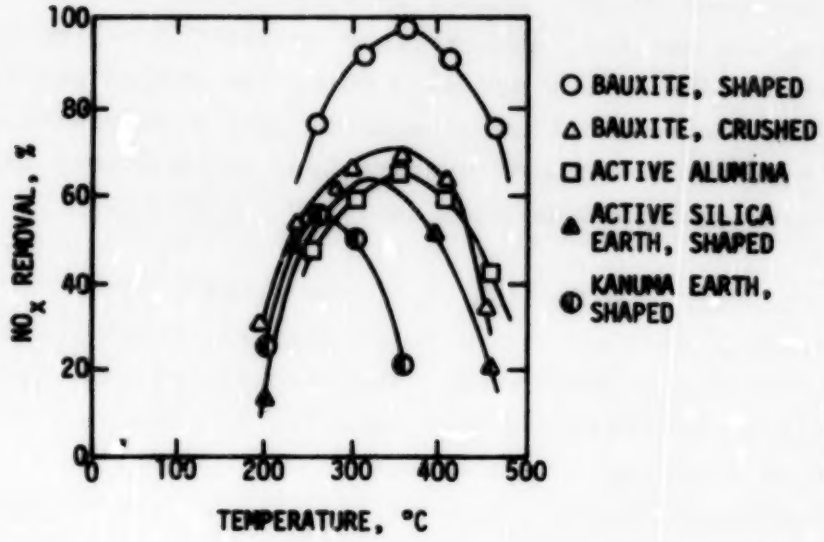


Figure 4-14. Tests on carriers (5% Cu).

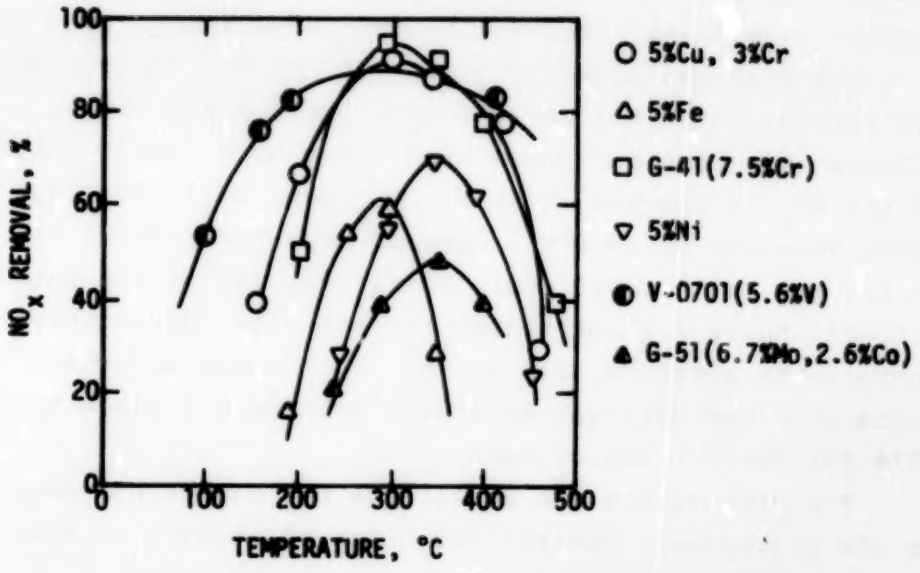


Figure 4-15. Tests of catalysts (alumina carrier).

which had been ground, shaped into cylinders (2.6 mm in diameter and height), and calcined at 550°C for 3 hours. The active alumina was not as good as the shaped bauxite. Since the characteristics of alumina vary widely with impurities and methods of preparation, it is likely that the alumina carrier will be much improved.

TOKYO ELECTRIC - MITSUBISHI H.I. SCR PROCESS

Process developers are Tokyo Electric Power Co. and Mitsubishi Heavy Industries. These companies have jointly operated a pilot plant with a capacity of treating 10,000 Nm^3/hr of flue gas from a natural-gas-fired boiler at the Minamiyokohama Station, Tokyo Electric. A process flowsheet is shown in Figure 4-16. Flue gas from an economizer is injected with ammonia, mixed in a mixer, and led to a reactor with a base-metal catalyst. Flue gas temperature fluctuates between 270 and 350°C as the boiler load varies between 25 and 100 percent. Efforts have been concentrated on development of a catalyst effective in the above temperature range.

The flue gas contains 90 to 100 ppm NO_x (mainly NO), 8.5 percent CO_2, 16.8 percent H_2O, and 2.6 percent O_2. A catalyst has been developed with which more than 80 percent of the NO_x is removed at an NH_3/NO_x mole ratio of 1 and a space velocity of 10,000. Ammonia concentration in the outlet gas is 10 to 20 ppm. Continuous use of the catalyst for 3000 hours did not reduce the activity appreciably. No increase in pressure drop in the reactor was observed. Tests on a new catalyst have been carried out since November 1974 for further improvement.

The process has the advantages and disadvantages common to SCR processes. Further reduction of ammonia in the outlet gas is desired.

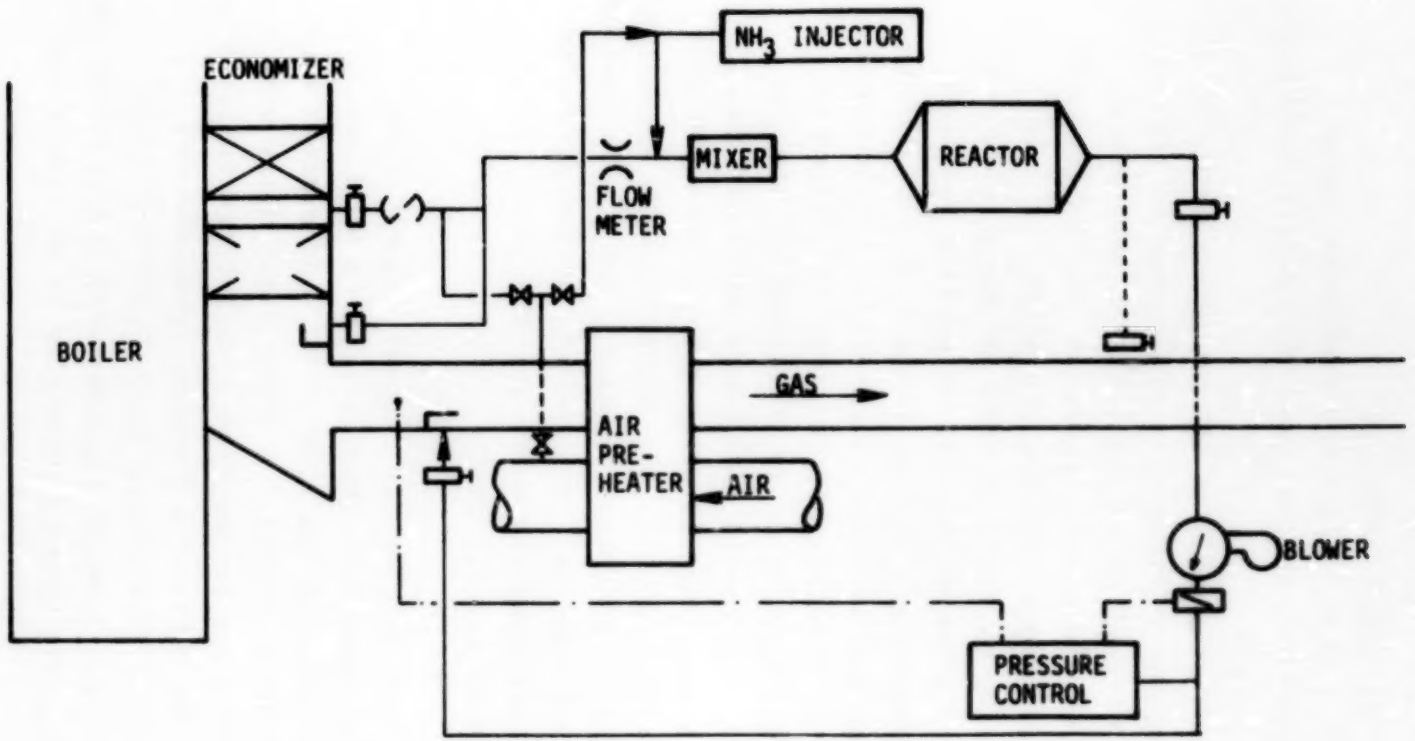


Figure 4-16. Flowsheet of pilot plant.
(Tokyo Electric - MHI SCR process)

SCR TESTS AT CHUBU ELECTRIC POWER

Chubu Electric Power, one of the nine major power companies, has conducted tests on two types of SCR processes.

Chubu-IHI-Mitsui Process

Chubu Electric has tested an SCR process jointly with Ishikawajima Harima Heavy Industries (IHI), one of the largest producers of boilers and machines; Mitsui Toatsu Chemical, the largest fertilizer producer; and Mitisui and Co., one of the two largest trading companies. A pilot plant with a capacity of treating 8000 Nm^3/hr of flue gas from a boiler burning low-sulfur oil or naphtha has been operated at the Shinnagoya Station, Chubu Electric, since October 1974. Flue gas is taken after either the economizer or the electrostatic precipitator to study the effect of dust. A simple dust eliminator is installed for the gas from the economizer. A nearly continuous operation for 2 months resulted in more than 90 percent NO_x removal without an increase in pressure drop in the reactor caused by the dust. The catalyst is resistant to SO_2. Most of the ammonia is decomposed in the reactor. The budget for the pilot test is $1.4 million, including the costs for the plant, labor, and everything needed for the test.

Chubu-MKK process

Chubu has tested another SCR process jointly with Mitsubishi Chemical Machinery (MKK) in search of a new catalyst that promotes the reaction of NO_x and ammonia at a low temperature (200 to 250°C). A small pilot plant with a capacity of treating 300 Nm^3/hr from an oil-fired boiler has been operated at the Yokkaichi Station, Chubu Electric, since September 1974. The budget is $100,000 excluding labor costs. Flue gas from an electrostatic precipitator is used for the test. The primary objective is to reduce the

energy requirement for reheating the gas after wet-process desulfurization. MKK recently started to use a catalyst made of iron oxide, which is said to be resistant to SO_2 and works fairly well at the low temperature.

OTHER CATALYTIC REDUCTION PROCESSES

Kansai Electric Power

Kansai Electric Power Co., one of the nine major power companies, has conducted tests on SCR jointly with Hitachi Ltd., one of the biggest machine producers. A pilot plant with a capacity of treating 4000 Nm^3/hr of flue gas from an oil-fired boiler (economizer outlet) has been operated since January 1974 at the Sakaiminato Station, Kansai Electric. Either crude or low-sulfur oil is burned in the boiler. The first test was carried out for 4200 hours between January and August 1974, removing more than 80 percent of the NO_x. At the beginning of the test, dust in the gas caused some problems that were gradually solved. After November 1974 the plant was partly modified, and the second test was started. No details have been disclosed. The process seems to have the advantages and disadvantages common to SCR processes.

Mitsubishi Heavy Industries

Since December 1974 MHI has operated a pilot plant with a capacity of treating 4000 Nm^3/hr of flue gas from an oil-fired boiler by SCR in conjunction with a wet desulfurization process. No data have been disclosed.

Osaka Oxygen Industries

Osaka Oxygen Industries (12-4, 2-chome, Utajima, Nishiyodogawa-ku, Osaka) constructed four commercial plants, each with a capacity of decolorizing 100,000 Nm^3/hr of flue gas from a natural-gas-fired power generation engine by

nonselective catalytic reduction using a noble-metal catalyst developed by Engelhard, U.S.A. The flue gas contains about 10 percent O_2 and 500 to 600 ppm NO_x, including a considerable amount of NO_2. The noble-metal catalyst is more active than a base-metal catalyst but is poisoned by SO_2.

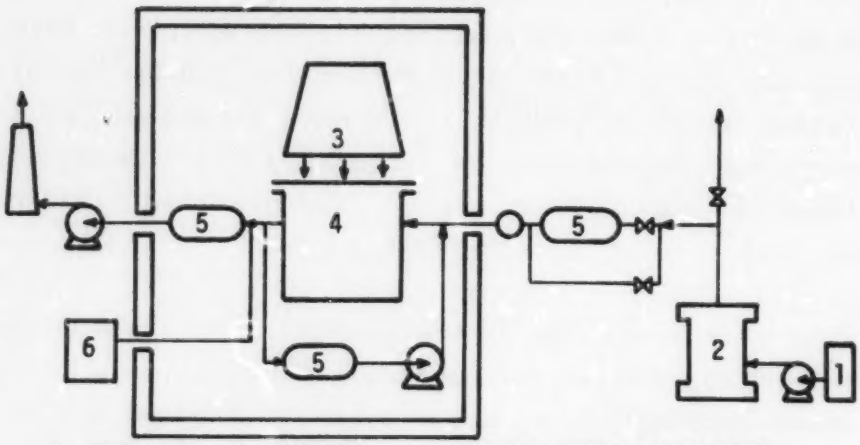
EBARA-JAERI ELECTRON BEAM PROCESS[12]

Background

The process developers are Ebara Manufacturing Co. and Japan Atomic Energy Research Institute (JAERI). Ebara is a large producer of water-treatment facilities that recently went into the air pollution control business. Ebara, jointly with JAERI, a government organization, has developed a process for simultaneous removal of SO_2 and NO_x by electron beam radiation. Following bench-scale tests, Ebara has operated a pilot plant with a capacity of treating 1000 Nm^3/hr of flue gas from an oil-fired boiler. A larger pilot plant with a capacity of treating 3000 Nm^3/hr of waste gas from an iron-ore sintering plant is scheduled to be constructed in 1976 at Yahata Works, Nippon Steel Corp.

Process Description

A flow sheet of a bench-scale test unit is shown in Figure 4-17. The reactor, 750 by 50 by 500 mm, is made of stainless steel. An electron beam accelerator (Cockcroft-Walton type) made by Hitachi, Ltd., was used. Flue gas produced by burning oil and containing 600 to 900 ppm SO_2 and 80 ppm NO_x passed through an electrostatic precipitator and into the reactor where it was exposed to the electron beam. Electron bombardment produces sulfuric acid mist and a powdery product and caught by another electrostatic precipitator.



1: FUEL OIL 2: BURNER 3: ELECTRON BEAM ACCELERATOR

4: REACTOR 5: DUST COLLECTOR 6: ANALYZER (SO_2, NO_x)

Figure 4-17. Apparatus for tests.

Figure 4-18 shows the results of the tests at 110°C. About 90 percent of the NO_x was removed by an electron beam of about 0.8 Mrad (radiation for 2 seconds of the beam with an intensity of 4.31×10^5 rad/sec), while about 80 percent of SO_2 was removed at 4 Mrad (radiation of the beam for 10 seconds). Radiation at lower temperature increased the removal efficiency slightly. The form of the product compound is not known.

The larger pilot plant (3000 Nm^3/hr) will cost more than $1 million, including equipment for various tests and measurements. Power consumption for the electron beam accelerator is estimated at 1 MW for 100,000 Nm^3/hr of flue gas (about 32 MW equivalent). It may be possible to make an electron beam accelerator as large as 1 MW. Consequently, treatment of 1,000,000 Nm^3/hr of flue gas from a 320-MW boiler will require 10 accelerators.

Evaluation

The main advantage of the process is the simultaneous removal of NO_x and SO_2 by consuming electric power only. The power consumption is not very high compared with that of other processes, which also require ammonia, lime, etc. The investment cost, however, seems fairly high, since the process requires accelerators and a highly efficient electrostatic precipitator. The by-product must be treated in a large-scale operation.

OTHER DRY PROCESSES

Sumitomo Shipbuilding Activiated-Carbon Process

Sumitomo Shipbuilding and Machinery Co., Ltd. developed an SO_2 removal process with activated carbon and constructed a prototype plant with a capacity of treating 175,000 Nm^3/hr of flue gas from an oil-fired boiler. Sumitomo has tested

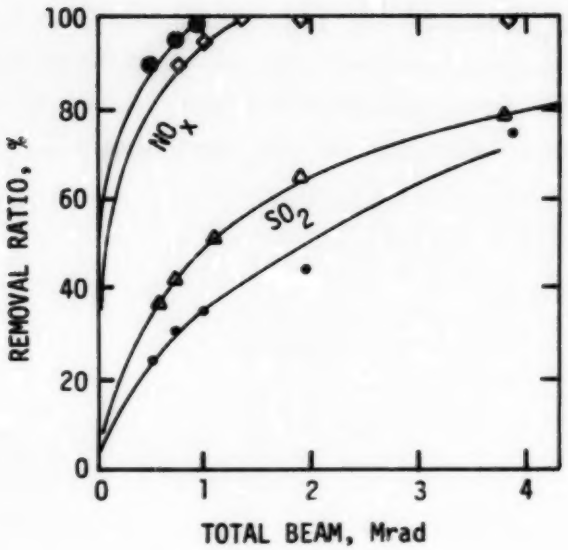


Figure 4-18. Results with different intensities.

NO_x removal with activated carbon using ammonia. No data have been disclosed.

Shell Cupric Oxide Process

Japan Shell Technology Co. constructed a desulfurization unit with a capacity of treating 120,000 Nm^3/hr of flue gas from an oil-fired boiler using the Shell cupric oxide process at the Yokkaichi Refinery, Showa Yokkaichi Sekiyu. Japan Shell has tested NO_x removal by injecting ammonia into a reactor containing cupric oxide. It is said that a high NO_x removal ratio can be attained because the copper oxide acts as a catalyst for the reaction of NO_x and ammonia. No data have been disclosed.

REFERENCES

Descriptions in this report are based primarily on the authors' visits to the denitrification plants, their discussions with the users and developers of each process, and data made available by them. In addition, the following publications were used as references:

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